DRAFT FOR
PUBLIC COMMENTS

ÉBAUCHE POUR
COMMENTAIRES DU PUBLIC

Canadian Environmental Protection Act, 1999

PRIORITY SUBSTANCES LIST

ASSESSMENT REPORT

AMMONIA IN THE AQUATIC ENVIRONMENT

Environment Canada
Health Canada

May 2000

TABLE OF CONTENTS

SYNOPSIS **8**

1.0 INTRODUCTION **11**

2.0 SUMMARY OF INFORMATION CRITICAL TO ASSESSMENT OF "TOXIC" UNDER CEPA 1999 .... **15**

2.1 IDENTITY AND PHYSICAL/CHEMICAL PROPERTIES 15
2.2 ENTRY CHARACTERIZATION 17
2.2.1 Production and use *17*
2.2.2 Sources and releases *18*
2.2.2.1 Natural sources 18
2.2.2.2 Anthropogenic sources 18
2.2.2.2.1 Industrial 18
2.2.2.2.2 Municipal 19
2.2.2.2.3 Combined sewer overflows 21
2.2.2.2.4 Agricultural 21
2.3 EXPOSURE CHARACTERIZATION 24
2.3.1 Environmental fate *24*
2.3.1.1 Air 25
2.3.1.2 Surface water 27
2.3.1.3 Soil and groundwater 29
2.3.2 Environmental concentrations *30*
2.3.2.1 Air 30
2.3.2.2 Atmospheric deposition 32
2.3.2.2.1 Case study: The Lower Fraser Valley 34
2.3.2.3 Surface water 36
2.3.2.4 Soil runoff 39
2.3.2.5 Soil 41
2.3.2.6 Groundwater 41
2.4 EFFECTS CHARACTERIZATION 41
2.4.1 Effects on terrestrial plants *41*
2.4.2 Acute effects on freshwater organisms *42*
2.4.2.1 Algae 42
2.4.2.2 Fish 43
2.4.2.3 Invertebrates 44
2.4.3 Sublethal effects on freshwater organisms *45*
2.4.4 Acute and sublethal effects on saltwater organisms *46*
2.4.4.1 Acute toxicity 47
2.4.4.2 Sublethal toxicity 49
2.4.5 Ecosystem effects *49*
2.4.5.1 Freshwater eutrophication 49
2.4.5.2 Coastal marine eutrophication 50
2.4.5.3 Terrestrial eutrophication 51

2.4.5.4 Acidification 52
2.4.6 Abiotic effects mediated through the atmosphere 52
2.5 TOXICOKINETICS, MODE OF ACTION AND METABOLISM 53
2.5.1 Freshwater fish 53
2.5.2 Marine fish 54
2.5.3 Accumulation in aquatic organisms 54
2.5.4 Factors affecting the aquatic toxicity of ammonia 54
2.5.4.1 pH 55
2.5.4.2 Temperature 55
2.5.4.3 Dissolved oxygen concentration 56
3.0 PROPOSED ASSESSMENT OF "TOXIC" UNDER CEPA 1999 57
3.1 CEPA 1999 64(A): ENVIRONMENT 57
3.1.1 Assessment endpoints 57
3.1.2 Environmental risk characterization 58
3.1.2.1 Hyperconservative assessments 58
3.1.2.2 Conservative assessments 59
3.1.2.2.1 Releases to air 59
3.1.2.2.2 Releases to water 62
3.1.2.2.3 Other lines of evidence 72
3.1.2.3 Probabilistic risk assessment 75
3.1.2.3.1 Hamilton Harbour 75
3.1.2.3.2 North Saskatchewan River 81
3.1.2.3.3 Red River 85
3.1.2.4 Discussion of uncertainty 93
3.1.2.5 Interpretation of ecological significance 96
3.2 CEPA 1999 64(B): ENVIRONMENT UPON WHICH LIFE DEPENDS 98
3.3 PROPOSED CONCLUSIONS 98
3.4 CONSIDERATIONS FOR FOLLOW-UP (FURTHER ACTION) 98
4.0 REFERENCES 100
APPENDIX A: AMMONIA EMISSIONS TO AIR FOR CANADA 118
APPENDIX B: PROVINCIAL BREAKDOWN OF AMMONIA RELEASES FROM NPRI (1996) 121
APPENDIX C: TOP 12 URBAN CENTRES FOR AMMONIA LOADING RATE (TONNES/YEAR) IN 1995 OR 1996 122
APPENDIX D: DEVELOPMENT OF EXPOSURE CDFS FOR THE NORTH SASKATCHEWAN RIVER 123
APPENDIX E: DEVELOPMENT OF EXPOSURE CDFS FOR THE RED RIVER 124
APPENDIX F: SEARCH STRATEGIES EMPLOYED FOR IDENTIFICATION OF RELEVANT DATA 125

LIST OF TABLES

Table 1: Physical and chemical properties of ammonia 16
Table 2: Percentage of total ammonia present as NH_3 in aqueous ammonia solutions 16
Table 3: Atmospheric ammonia and ammonium aerosol concentrations at various locations 31
Table 4: Mean LC_{50}s for un-ionized ammonia in Canadian fish species 44
Table 5: Mean LC_{50}s for un-ionized ammonia in invertebrate species 45
Table 6: Summary of mean sublethal endpoints in freshwater species 46
Table 7: Ranked mean acute toxicity values for un-ionized ammonia 48
Table 8: Ammonia connections to other air issues 53
Table 9: Summary of hyperconservative assessments 59
Table 10: Summary of conservative assessment of modelled sewage treatment systems 69
Table 11: Summary of conservative assessments for agricultural runoff situations 70
Table 12: Probability of species affected 1–20 km downstream of the wastewater treatment plant on the North Saskatchewan River in August 84
Table 13: Probabilities of impacts at four sites around Winnipeg 93

LIST OF FIGURES

Figure 1: The nitrogen cycle 24
Figure 2: Fate analysis of ammonia in the atmosphere 27
Figure 3: Fate analysis of ammonia in aquatic environments 29
Figure 4: Dispersion of NH_3 downwind of a feedlot 33
Figure 5: Ammonia air emissions inventory for the Lower Fraser Valley, 1996–1997 35
Figure 6: Modelled total nitrogen deposition (kg/ha per year) for the Lower Fraser Valley 36
Figure 7: Un-ionized ammonia concentrations upstream and downstream of Edmonton 37
Figure 8: Acute ACRM for Canadian freshwater species 63
Figure 9: Chronic ACRM for Canadian species listed in Table 6 64
Figure 10: Discharge of Toronto municipal effluent into Lake Ontario, September 1998 66
Figure 11: North Saskatchewan River in the vicinity of Edmonton 73
Figure 12: Hamilton Harbour 76
Figure 13: Seasonal fluctuations in ammonia (mg/L) at the central station in Hamilton Harbour77
Figure 14: Total and un-ionized ammonia concentrations at the central station in Hamilton Harbour, 1-m depth 78
Figure 15: Un-ionized ammonia concentrations in Windermere Arm, Hamilton Harbour 79
Figure 16: Risk curve for un-ionized ammonia at the central station in Hamilton Harbour 80
Figure 17: Cumulative density function of NH_3 concentrations for August at 1 km along the centre of the plume in the North Saskatchewan River 82
Figures 18–23: Risk curves for 1–20 km downstream of the wastewater treatment plant on the North Saskatchewan River 83
Figure 24: Probability of impacts in the North Saskatchewan River 84
Figure 25: Winnipeg sewage treatment plants and sample sites 86
Figure 26: Red River monthly mean flows and total ammonia concentrations 87
Figure 27: Un-ionized ammonia concentrations in the Red River at Lockport Dam, north of Winnipeg 88

Figures 28–31: Risk curves for Fort Garry, Red River 89
Figures 32–35: Risk curves for Perimeter Bridge, Red River 90
Figures 36–39: Risk curves for Lockport Dam, Red River 91
Figures 40–43: Risk curves at Main Street Bridge, Assiniboine River 92
Figure 44: Cumulative density function for Red River at Fort Garry Bridge, August 124

LIST OF ACRONYMS AND ABBREVIATIONS

ACRM	Aquatic Community Risk Model
CAS	Chemical Abstracts Service
CDF	cumulative density function
CEPA 1999	*Canadian Environmental Protection Act, 1999*
CTV	Critical Toxicity Value
DO	dissolved oxygen
EC_{20}	20% effective concentration
EC_{50}	median effective concentration
ET_{50}	time to 50% effect
EEV	Estimated Exposure Value
ENEV	Estimated No-Effects Value
IC_{20}	concentration causing 20% inhibition in exposed organisms
ISCST3	Industrial Source Complex Short Term model
ISOPART	Inorganic and Secondary Organic Particle model
LC_{10}	10% lethal concentration
LC_{50}	median lethal concentration
LT_{50}	time to 50% mortality
$PM_{2.5}$	particulate matter less than or equal to 2.5 µm in diameter
PM_{10}	particulate matter less than or equal to 10 µm in diameter
N	nitrogen
NH_3	un-ionized ammonia
NH_4^+	ionized ammonia
NPRI	National Pollutant Release Inventory
PSL	Priority Substances List
REVEAL	Regional Visibility Experimental Assessment in the Lower Fraser Valley
U.S. EPA	United States Environmental Protection Agency
VOC	volatile organic chemical
WWTP	municipal wastewater treatment plant

SYNOPSIS

Ammonia exists in two forms simultaneously, with the equilibrium between the two forms governed in large part by pH and temperature. The forms are NH_3 (un-ionized ammonia) and NH_4^+ (ionized ammonia or ammonium). Together they are called total ammonia. It is the NH_3 form that is particularly harmful to aquatic organisms. The formation of NH_3 is favoured at higher pHs but is also affected by temperature. This means that while the concentration of total ammonia may remain constant in a water body, the proportion of un-ionized ammonia fluctuates with temperature and pH. Significant formation of NH_3 can occur within a single day as water temperatures fluctuate.

Ammonia evaporates at temperatures above –33°C and will travel short distances (several kilometres) as a gas. It readily forms ammonium sulphate particles in air when in the presence of sulphur compounds; in this form, it can travel hundreds of kilometres.

In 1996, ammonia was ranked first by the National Pollutant Release Inventory in terms of amounts released by industry to the Canadian environment. Just over 32 000 tonnes were reported as released by industries across Canada to all media (air, water and land). Ammonia is also a naturally occurring compound required by most organisms for protein synthesis and a waste product of animal, fish and microbial metabolism. The primary human use of ammonia is as a nitrogen source in fertilizers, especially anhydrous ammonia and urea.

Ammonia is released into the environment by many industries and other human activities. The major quantifiable sources of ammonia released to aquatic ecosystems across Canada are municipal wastewater treatment plants (WWTPs). The amount of ammonia released to water via municipal WWTPs is estimated at 62 000 tonnes/year. Negative environmental impacts on some aquatic ecosystems are occurring from this source.

Agricultural releases of ammonia to water cannot be quantified because of the diffuse nature of agriculture in Canada and the difficulty in quantifying such releases. In general, only those intensive animal-rearing facilities (feedlots and dairies) with direct runoff to watercourses have the potential to significantly contaminate the water.

Industrial releases to water amount to 5972 tonnes/year. The major industries are pulp and paper mills, mines, food processing and fertilizer production.

The major industrial source of ammonia released to the atmosphere is the fertilizer industry, releasing some 12 000 tonnes/year. In contrast, the amount of ammonia released to air from agricultural operations is estimated at 700 000 tonnes/year. Through modelling and measuring ammonia deposition in areas influenced by agricultural emissions and studying the situation in Europe, it was determined that some areas of Canada, like the Lower Fraser Valley, are potential impact regions.

It was determined from reviewing toxicity and exposure data that freshwater organisms are most at risk from releases of ammonia in the aquatic environment. Rainbow trout, freshwater scud, walleye, mountain whitefish and fingernail clams are some of the most sensitive species.

Aquatic insects and micro-crustaceans are more resistant to ammonia, although there is a large variation in sensitivity within aquatic insects.

The ecological impact of ammonia in aquatic ecosystems is likely to occur through chronic toxicity to fish and benthic invertebrate populations as a result of reduced reproductive capacity and reduced growth of young. These are subtle impacts that will likely not be noticed for some distance below an outfall. The zone of impact varies greatly with discharge conditions, river flow rate, temperature and pH. Under estimated average conditions, some municipal wastewater discharges could be harmful for 10–20 km. Severe disruption of the benthic flora and fauna has been noted below municipal wastewater discharges. Recovery may not occur for many (20–100) kilometres. It is not clear whether these impacts are solely from ammonia or from a combination of factors, but ammonia is a major, potentially harmful constituent of municipal wastewater effluents.

Owing to the interaction between receiving water pH and temperature, those waters most at risk from municipal wastewater-related ammonia are those that are routinely basic in pH with a relatively warm summer temperature combined with low flows. In Canada, winter temperatures, regardless of pH, are low enough to keep the formation of un-ionized ammonia below the toxic threshold. Potentially toxic conditions typically start in May and can continue through to early October, depending on the water system and the yearly variation in pH, dissolved oxygen and temperature. In general, waters potentially sensitive to ammonia from municipal WWTPs are found in southern areas of Alberta, Saskatchewan and Manitoba; southern Ontario; and the south shore of Quebec.

Ammonia is generally not problematic with respect to the eutrophication of fresh waters in Canada, as this is typically limited by phosphorus. There are a few exceptions to this, in particular the Qu'Appelle Lakes in Saskatchewan. Ammonia released by the Regina WWTP, coupled with phosphorus mobilization from sediments, seems to be contributing to the continued eutrophication of this lake system.

Conifer trees are sensitive to ammonia exposure from air, particularly in winter. They develop a reduction in winter hardiness due to an impaired ability to retain water. The beneficial mycorrhizal fungi that colonize many types of plant roots are particularly sensitive to ammonia. Reductions in mycorrhizal fungi on tree roots may be the reason for reduced water retention in conifers. Conifer forests and sphagnum bogs are particularly at risk if sufficient ammonia is added over time. Conifers may experience a form of eutrophication, and sphagnum cannot compete with grasses under increased ammonia conditions.

Ammonia is not involved in the formation of ground-level ozone, the depletion of stratospheric ozone or climate change.

Based on probabilistic risk assessments of three water bodies receiving ammonia from typical municipal wastewater discharges, ammonia is considered to be entering the aquatic environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. Based on available data, it is concluded that ammonia is not entering the

environment in a quantity or concentration or under conditions that constitute or may constitute a danger to the environment on which life depends. Thus, it is proposed that ammonia in the aquatic environment be considered "toxic" as defined in Section 64 of the *Canadian Environmental Protection Act, 1999* (CEPA 1999).

As the conclusion of this assessment is based on analyses of risks posed by releases of ammonia from municipal WWTPs, priority should be given to consideration of options to reduce exposure to ammonia from municipal wastewater systems. Results of conservative screening-level assessments suggest that releases of ammonia from several other sources (e.g., runoff from manure-fertilized fields and intensive livestock operations) may also be causing environmental harm; however, available data were insufficient to establish the extent and magnitude of such harm. It is recommended that additional data be obtained to determine whether options to reduce exposure to ammonia from such sources should be undertaken.

1.0 INTRODUCTION

The *Canadian Environmental Protection Act, 1999* (CEPA 1999) requires the federal Ministers of the Environment and of Health to prepare and publish a Priority Substances List (PSL) that identifies substances, including chemicals, groups of chemicals, effluents and wastes, that may be harmful to the environment or constitute a danger to human health. The Act also requires both Ministers to assess these substances and determine whether they are "toxic" or are capable of becoming "toxic" as defined in Section 64 of the Act, which states:

> … a substance is toxic if it is entering or may enter the environment in a quantity or concentration or under conditions that
> (a) have or may have an immediate or long-term harmful effect on the environment or its biological diversity;
> (b) constitute or may constitute a danger to the environment on which life depends; or
> (c) constitute or may constitute a danger in Canada to human life or health.

Substances that are assessed as "toxic" as defined in Section 64 may be placed on Schedule I of the Act and considered for possible risk management measures, such as regulations, guidelines, pollution prevention plans or codes of practice to control any aspect of their life cycle, from the research and development stage through manufacture, use, storage, transport and ultimate disposal.

Based on initial screening of readily accessible information, the rationale for assessing ammonia in the aquatic environment provided by the Ministers' Expert Advisory Panel on the Second Priority Substances List (Ministers' Expert Advisory Panel, 1995) was as follows:

> Anthropogenic sources of ammonia in Canada include effluent from sewage treatment plants, steel mills, fertilizer plants, the petroleum industry and intensive farming. Releases from these sources can result in locally elevated concentrations. At several point sources in Canada, concentrations exceed the threshold levels of sensitive species such as rainbow trout. An assessment of ammonia in the aquatic environment is needed to evaluate the extent of the problem.

Following an initial scoping exercise, it was decided that the scope of the assessment was too narrow and that it should be expanded to include the atmospheric and terrestrial environments in Canada. This decision was based on the findings of European researchers that ammonia transmitted by air to sensitive terrestrial ecosystems was having negative impacts on those ecosystems. Several of the impacted European ecosystems, conifer forests in particular, exist in large areas of Canada. Also, the atmospheric chemistry of ammonia is such that its interactions with sulphates form fine respirable particulate matter ($PM_{2.5}$ and PM_{10}). Since "Respirable particulate matter less than or equal to 10 microns" (i.e., PM_{10}) has been determined to be CEPA "toxic" to humans, an evaluation of the role of ammonia in the formation (but not the environmental effects) of respirable particulate matter was warranted.

A description of the approaches to assessment of the effects of Priority Substances on the environment is available in a published companion document. The document, entitled "Environmental Assessments of Priority Substances under the *Canadian Environmental Protection Act*. Guidance Manual Version 1.0 — March 1997" (Environment Canada, 1997a), provides guidance for conducting environmental assessments of Priority Substances in Canada. This document may be purchased from:

Environmental Protection Publications
Environmental Technology Advancement Directorate
Environment Canada
Ottawa, Ontario
K1A 0H3

It is also available on the Internet at www.ec.gc.ca/cceb1/eng/psap.htm under the heading "Technical Guidance Manual." It should be noted that the approach outlined therein has evolved to incorporate recent developments in risk assessment methodology and which will be addressed in future releases of the guidance manual for environmental assessments of Priority Substances.

The search strategies for identification of data relevant to assessment of potential effects on the environment (prior to January 1999) are presented in Appendix F. Review articles were consulted where appropriate. However, all original studies that form the basis for determining whether ammonia is "toxic" under CEPA 1999 have been critically evaluated by staff of Environment Canada (entry and environmental exposure and effects).

The Assessment Report was written by M. Constable, F. Jensen, K. McDonald, K. Taylor and M. Charlton (Canada Centre for Inland Waters) of Environment Canada. The Assessment Report and the supporting documentation (Environment Canada, 2000) related to the assessment of ammonia were reviewed by the following members of the Environmental Resource Group, established by Environment Canada to support the environmental assessment:

P. Chambers, National Water Research Institute, Environment Canada
G. Craig, GR Craig and Associates
P. Doyle, Environment Canada
J. Farrell, Canadian Fertilizer Institute
L. Gammie, Canadian Water and Wastewater Association
J. Haskill, Environment Canada
S. McGinn, Agriculture and Agri-Food Canada
J. McLernon, Environment Canada
D. Moore, The Cadmus Group, Inc.
B. Munson, Environment Canada
D. Penney, Alberta Agriculture
K. Reid, Ontario Ministry of Agriculture, Food and Regional Affairs
S. Sheppard, EcoMatters
W. Windle, Environment Canada

Environmental sections of the Assessment Report and supporting documentation (Environment Canada, 2000) were also reviewed by external reviewers:

J. Diamond, TetraTech Inc.
B. Parkhurst, The Cadmus Group, Inc.

The basis for recommending inclusion of ammonia in the aquatic environment by the Ministers' Expert Advisory Panel on the Second Priority Substances List was limited to environmental effects (namely, effects on sensitive aquatic species). As a result, the principal focus of this assessment is a determination of whether ammonia is "toxic" under Paragraph 64(a) of CEPA 1999. However, in view of the expansion of the scope of the assessment of environmental effects to address the terrestrial environment (through exposure via air) as well, effects of ammonia in air and water on human health were also considered, at least in a preliminary fashion, primarily to ensure that conclusions drawn on the basis of a more robust data set on environmental effects would also be protective of human health.

The database on the effects of ammonia relevant to assessment of the effects on human health is limited principally to early short-term studies in animals, older reports of accidental exposures of humans, limited clinical studies and one cross-sectional study of an occupationally exposed population (Health Canada, 1999). The paucity of information on effects in experimental animals and humans is likely attributable to the considerably greater amounts of ammonia produced endogenously in humans through metabolism in the synthesis of amino acids, nucleosides and other nitrogen-containing compounds compared with environmental exposure, as well as to its relatively low toxicity.

Because of the focus on environmental effects and in view of the limitations of the data relevant to assessment of the effects on human health, a screening assessment was conducted, in which the limited number of identified effect levels for ammonia in the more relevant studies were compared with worst-case or bounding estimates of exposure in air (including indoor air) and drinking water and the adequacy of these rather crude margins of exposure was considered. On the basis of the magnitude of these margins, which are considered sufficient to account for various elements of uncertainty and variability, ammonia is not considered a priority for investigation of options to reduce public exposure through control of sources that are addressed under CEPA (Health Canada, 1999), and the remainder of this assessment addresses effects on the environment. Unpublished supporting documentation on the health-related effects of ammonia in the aquatic environment, which presents additional information, is available upon request from:

Environmental Health Centre
Room 104
Health Canada
Tunney's Pasture
Ottawa, Ontario
K1A 0L2

Copies of this Assessment Report are available upon request from:

Inquiry Centre
Environment Canada
Main Floor, Place Vincent Massey
351 St. Joseph Blvd.
Hull, Quebec
K1A 0H3

or on the Internet at:

http://www.ec.gc.ca/cceb1/eng/public/index_e.html

Unpublished supporting documentation, which presents additional information, is available upon request from:

Commercial Chemicals Evaluation Branch
Environment Canada
14th Floor, Place Vincent Massey
351 St. Joseph Blvd.
Hull, Quebec
K1A 0H3

2.0 SUMMARY OF INFORMATION CRITICAL TO ASSESSMENT OF "TOXIC" UNDER CEPA 1999

2.1 Identity and physical/chemical properties

Ammonia terminology has been a source of confusion within the technical literature for years. Terms such as free ammonia, total ammonia, non-dissociated ammonia and un-ionized ammonia nitrogen are commonly encountered and tend not only to confuse the reader, but also to make comparison of the data difficult. To solve this problem, the definitions given below will be adhered to throughout this document.

In aqueous solutions, a chemical equilibrium is established between un-ionized ammonia (NH_3), ionized ammonia (NH_4^+) and hydroxide ions (OH^-). The equilibrium for these chemical species can be expressed in simplified form by the equation:

$$NH_3 + H_2O \leftrightarrow NH_3 \cdot H_2O \leftrightarrow NH_4^+ + OH^- \text{ or } NH_4OH$$

The term "***un-ionized ammonia***" refers to all forms of ammonia in water other than the ammonium ion (NH_4^+). In the literature, this has been designated as NH_3, NH_4OH and $NH_3 \cdot H_2O$. The expression NH_3 is used throughout this report to represent un-ionized ammonia, except in instances where one or the other expression is more appropriate to the context (e.g., see the chemical equilibrium discussion later in this section).

The term "***ionized ammonia***" refers to the ammonium ion, NH_4^+.

The terms "***total ammonia***" and "***ammonia***" refer to the sum of un-ionized ammonia and ionized ammonia ($NH_3 + NH_4^+$).

Ammonia is a colourless alkaline gas, lighter than air and possessing a unique penetrating odour. The name "ammonia" is a general term and refers to anhydrous ammonia, ammonia gas and ammoniac anhydre. Ammonia has the Chemical Abstracts Service (CAS) registry number 7664-41-7. The substance has the molecular formula NH_3 and a molecular weight of 17.03 (Grayson and Eckroth, 1978).

Considerable information about the properties of ammonia is given in WHO (1986) and Environment Canada (1984). The physical and chemical properties relevant to the environmental fate of ammonia are summarized in Table 1.

Table 1: Physical and chemical properties of ammonia

Property	Value
Boiling point at 100 kPa	–33.42°C
Melting point at 100 kPa	–77.74°C
Density (liquid) at –33.7°C and 100 kPa	682.8 kg/m^3
Density (gas) at 25°C	0.7067 kg/m^3
Vapour pressure at 15.5°C at 21°C at 25°C	 640 kPa[1] 880 kPa[1] 1000 kPa
pK$_a$ (25°C, pH 8)	9.24
Solubility in water, 101 kPa at 0°C at 20°C at 40°C at 60°C	 895 g/L 529 g/L 316 g/L 168 g/L

[1] Figure from literature review by Environment Canada (1984).

Using their pK$_a$ calculations, Emerson *et al.* (1975) developed a table (Table 2) describing the percentage of NH_3 in fresh or soft water for temperatures between 0 and 30°C and for pHs in the range 6.0–10.0.

Table 2: Percentage of total ammonia present as NH_3 in aqueous ammonia solutions

Temp. (°C)	PH								
	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
0	0.008	0.026	0.082	0.261	0.820	8.55	7.64	20.7	45.3
5	0.012	0.039	0.125	0.394	1.23	3.80	11.1	28.3	55.6
10	0.018	0.058	0.186	0.586	1.83	5.56	15.7	37.1	65.1
15	0.027	0.086	0.273	0.859	2.67	7.97	21.5	46.4	73.3
20	0.039	0.125	0.396	1.24	3.82	11.2	28.4	55.7	79.9
25	0.056	0.180	0.566	1.77	5.38	15.3	36.3	64.3	85.1
30	0.080	0.254	0.799	2.48	7.46	20.3	44.6	71.8	89.0

The relationship illustrated in Table 2 holds in most fresh waters. However, the concentration of un-ionized ammonia will be lower at the higher ionic strengths (total dissolved solids) of very hard fresh waters or saline waters. For a given total ammonia concentration, the concentration of un-ionized ammonia decreases slightly with increasing salt content, and this effect can be significant in estuarine and marine waters. Using the appropriate activity coefficients, this relationship can be restated for seawater with an ionic strength of 0.7 as follows (API, 1981):

$$f = 1/[10^{(pK_a - pH) + 0.221} + 1]$$

At 25°C, the pK_a is 9.24 (Emerson *et al.*, 1975), so at pH 8, the above equation shows that 3.3% of the total ammonia in seawater would exist in the un-ionized form. The corresponding value in fresh water is 5.4%. At this pH and temperature, seawater with an ionic strength of 0.7 contains 38% less un-ionized ammonia than does fresh water.

2.2 Entry characterization

2.2.1 Production and use

According to a marketing research report by Lauriente in 1995, Canada produced 3.0 million tonnes of ammonia in 1990 and 3.4 million tonnes in 1993. Exports of ammonia from Canada were significant compared with imports. In 1989 and 1993, respectively, 1.1 million tonnes and 0.84 million tonnes of ammonia were exported, while 2000 tonnes and <500 tonnes were imported (Lauriente, 1995).

The primary industrial use of ammonia is as the nitrogen source in fertilizers, with direct application of anhydrous ammonia being the largest single method of consumption. The Prairie provinces are the largest users of these products, consuming 81% of the nitrogen content sold (Korol and Rattray, 1998). Ammonium sulphate, ammonium nitrate, urea and ammonium phosphate are fertilizers produced from ammonia. To a lesser extent, ammonia is used in many industrial applications. Ammonia can be regarded as reduced nitric acid and is used in the production of many other substances. At petroleum refineries, ammonia is formed from catalyst regenerators in the fluid catalytic cracking process. Other uses of ammonia include the following:

- Manufacture of synthetic fibres (caprolactam for nylon), plastics and glues; pharmaceuticals, vitamins, amino acids, dentifrices, lotions and cosmetics; household ammonia, detergents and cleansers; numerous organic and inorganic chemicals, such as nitric acid, cyanides, amides, amines, nitrates, nitriles, hexamethylene diamine, ethanolamines, ammonium thiosulphate and dye intermediates.
- Production of explosives, rocket fuel, beer and nitrogen oxides required for manufacturing sulphuric acid, sugar purification and treatment and refinement of metals.
- Use as a refrigerant in both compression and absorption systems; a neutralizing agent for acids in oil protecting refinery equipment from corrosion; a flux for soldering; a treatment for wheat and barley straw as a supplement to sheep and cattle feed; a food additive; for growth and control of pH in yeast cultures; a latex preservative; a flame-proofing agent; a curing agent in leather making; a mothproofing agent; and as a reducing agent for nitrogen oxides in flue gas during steel production.
- Use as a dyeing agent, and preventing afterglow in matches.

2.2.2 Sources and releases

2.2.2.1 Natural sources

Much of the ammonia in the atmospheric environment is from natural sources. Since ammonia is continually released throughout the biosphere by the breakdown or decomposition of organic waste matter, any natural or industrial process that concentrates and makes nitrogen-containing organic matter available for decomposition represents a potential source of high local concentrations of ammonia.

Releases from natural processes that can be accounted for are approximately equal to the releases from the animal husbandry industry (see Appendix A). Each is responsible for the release of over 500 000 tonnes of ammonia to the atmosphere. The estimates of natural production and release to air are very approximate (Geadah, 1980; Vezina, 1997).

2.2.2.2 Anthropogenic sources

2.2.2.2.1 Industrial

Environment Canada conducts an annual survey of Canadian industries (National Pollutant Release Inventory [NPRI]) likely to be using or releasing pollutants, including ammonia (NPRI, 1996). Total reported industrial releases of ammonia in 1996 were 32 037 tonnes. This makes ammonia the top-ranked NPRI substance in terms of amounts released in Canada. The NPRI has strict reporting criteria, such that most municipal sewage treatment plants, very few animal husbandry systems and no transportation systems had to report. These are known to be some of the major anthropogenic sources of ammonia released to the Canadian environment.

Alberta released the largest quantity of ammonia in Canada in 1996, accounting for over half of the releases (17 665 tonnes to all media). This is due to the large number of fertilizer manufacturing facilities, pulp and paper mills and petroleum refineries in the province. Ontario released less than half of Alberta's releases (7552 tonnes), and Quebec released even less (1914 tonnes) (see Appendix B for details).

Industrial releases directly to watercourses totalled 5972 tonnes in 1996 and are typically from companies that are resource-based, such as pulp and paper, mining and coal-fired power generation, although a few significant releases come from heavy industries located in cities and from food processing. Fourteen companies were involved in pulp and paper manufacture in 1996, and these released a total of 1371 tonnes of ammonia that year. Three steel mills released 775 tonnes of ammonia, a single food processor released 504 tonnes, two fertilizer manufacturers released 180 tonnes, five mines released 537 tonnes and a coal-fired power generation plant released 62 tonnes. The rest (2543 tonnes) was released by many other industries.

Large releases in a city are usually due to one or two facilities. Hamilton, Ontario, is a major release site due to three steel-producing facilities. Other cities with significant industrial releases of ammonia are:

- Maitland, Ontario (fertilizer and chemical manufacture) — air and water releases,

- Toronto, Ontario (chemical and paper manufacture) — air and waste treatment releases,
- Medicine Hat, Alberta (fertilizer and chemical manufacture) — air and waste treatment releases,
- Brandon, Manitoba (fertilizer and chemical/pharmaceutical manufacture) — air and waste treatment releases, and
- Fort Saskatchewan, Alberta (fertilizer and chemical manufacture) — air and water releases.

The fertilizer industry is the largest industrial releaser of ammonia in Canada. Of the 10 largest industrial sources of ammonia listed in the 1996 NPRI report, six are fertilizer manufacturers. Three are located in Alberta, at Redwater, Medicine Hat and Calgary, one in Manitoba, at Brandon, and two in Ontario, at Courtright and Maitland. Together they released 12 302 tonnes out of 32 037 tonnes reported, which is 38% of the total released. Most of these releases are to air.

The metal foundry industry is located primarily in Ontario. Of the largest ammonia sources in this sector, the top releasers are Algoma Steel in Sault Ste. Marie, Ontario (676 tonnes); the Cobalt Refinery Company, Fort Saskatchewan, Alberta (528 tonnes); the Inco Nickel Refinery, Copper Cliff, Ontario (297 tonnes); the Stelco refinery, Hamilton, Ontario (182 tonnes); and the Dofasco refinery, Hamilton, Ontario (180 tonnes). There are significant differences in the releases, however. The Inco and Cobalt facilities release nearly all of their ammonia to the air, Algoma Steel releases most of its ammonia to water, and the Stelco and Dofasco facilities split their releases between air and water. Other metal-working facilities, such as Stelwire of Hamilton, Ontario, produce large quantities of ammonia (245.5 tonnes), but they send all of it to the local municipal wastewater treatment plant (WWTP), so their releases will show under the municipal wastes for Hamilton.

The petroleum extraction and refining industry is a relatively large source of ammonia. The largest releasers within this sector in 1996, all in Alberta, were the Shell Scotford refinery, Fort Saskatchewan (2488 tonnes), Petro Canada refinery, Edmonton (1718 tonnes), and Imperial Oil Limited Strathcona refinery, Edmonton (1130 tonnes). However, their releases of ammonia are primarily to deep-well disposal, very little being released to surface waters. Following these are the Syncrude Canada Mildred Lake Site near Fort McMurray, Alberta (454 tonnes), and the Ultramar Ltée. Raffinerie de St-Romuald, in St-Romuald, Quebec (229 tonnes). Syncrude does not have a reported release, as it uses massive retention ponds.

2.2.2.2.2 Municipal

Four sources of information were used to determine releases of ammonia from municipal sewage treatment plants. Environment Canada issued a voluntary survey to municipalities in all provinces (Environment Canada, 1997b) except Quebec (at their request) to collect information on effluent flow rates and releases of ammonia to local watercourses. Also requested was information on the quantities and ammonia content of sewage sludge and sludge disposal methods. The Ontario Ministry of Environment and Energy (OMEE, 1997) provided a copy of its municipal discharge database, which includes data on ammonia concentrations from all municipalities in Ontario. This was combined with Environment Canada's Municipal Water Use Database (Environment Canada, 1997c), which contains information on flow rates with which to calculate loading rates of ammonia from Ontario municipalities. A survey of 15 communities in Quebec provided ammonia release data and flow rates for a 3-day period in 1996 and 1997 (MEFQ, 1998). The average ammonia concentration in sewage effluents reported to Environment Canada (1997b) was 13.89 mg/L.

A survey of water usage by Canadian municipalities indicates that sewage treatment plants are a large source of ammonia to the aquatic environment. Average daily flow rates from all municipalities in Canada for 1994 were 12.3×10^6 m^3/day (Environment Canada, 1997c). This equates to 4.49×10^{12} L/year. With an estimated average total ammonia concentration of 13.89 mg/L in domestic sewage (Environment Canada, 1997b), the estimated load to aquatic systems is 62 000 tonnes/year.

As the Environment Canada survey of municipalities was not exhaustive, being voluntary, the tonnage of ammonia released is a conservative estimate. Also, many treatment facility operators did not know the concentration of ammonia in their effluent and so did not provide those data. A figure of 13.89 mg/L (the national average) was used to estimate releases from these facilities.

The current knowledge of the quantities of ammonia disposed of in sewage sludge is not very good. The municipal survey did include questions on quantities of sludge produced and ultimate disposal methods; however, the answers received were of low quality. Many facilities record quantities of sludge in volumes, while others record weights. Many do not know the concentrations of ammonia in the sludge. An estimate of 5722 tonnes of ammonia disposed of in sludge was generated, based on 1222 tonnes of ammonia reported and 4500 tonnes extrapolated from the reports. The average ammonia concentration reported in sludge was 2200 mg/kg, with a range of 0.29–38 600 mg/kg.

Appendix C summarizes the ammonia loading rates for the top 12 urban centres in 1995–1996. Montréal has the highest ammonia loading rate of any city in Canada. This is due to an effluent flow rate twice that of Toronto, although its effluent is surprisingly dilute for a primary treatment system. Montréal's loading rate of 6128 tonnes/year to the St. Lawrence River is nearly the same as Toronto's, at 5938 tonnes/year released to Lake Ontario. Vancouver is the next largest releaser of ammonia (5741 tonnes/year to the Fraser River and Strait of Georgia), as its effluents are moderately high in ammonia and have a high flow rate. The four Vancouver facilities have either primary or secondary treatment. Winnipeg is fourth because of its very high ammonia concentration, averaging 26 mg/L in 1995, giving it a loading rate of 2152 tonnes/year to the Red River. Edmonton is fifth, but by 2005 Edmonton's loading rate should be at least half of what it is currently, as the city is installing a nitrification/denitrification process. Many urban centres have several sewage treatment facilities; for these calculations, their effluent flows and ammonia concentrations have been flow weighted and aggregated.

A comparison was made of industrial releases directly to water and municipal releases to water. The ammonia from municipal effluents in any province far outweighs the industrial discharges of ammonia to water.

2.2.2.2.3 Combined sewer overflows

Combined sewer overflows occur when stormwater drains are routed into the sewage system, so that the sewage treatment system is overloaded during a large rain event. When overloading occurs, raw sewage is diverted directly into the receiving water along with the stormwater.

Mean concentrations of ammonia in stormwater estimated for three Ontario cities — Sarnia, Sault Ste. Marie and Windsor — were 0.5, 0.7 and 0.3 mg NH_3/L, respectively (Marsalek and Ng, 1989). Ammonia concentrations in municipal wastewater effluents were 75.4, 181.5 and 27.7 mg/L, respectively. Concentrations were calculated from point source loadings that were divided by the annual volume of stormwater runoff (UGLCC, 1988a,b,c). When comparing loadings in the stormwater with those in combined sewer overflows, overflows exceeded stormwater in loadings of ammonia in both Sarnia and Windsor, despite the fact that stormwater discharges in Sarnia and Windsor were 6.7×10^6 and 22.3×10^6 m^3/year, respectively, and the volumes of combined sewer overflow in Sarnia and Windsor were 1.0×10^6 and 5.2×10^6 m^3/year, respectively (Marsalek and Ng, 1989).

2.2.2.2.4 Agricultural

Manure application

Few, if any, agricultural operations track ammonia emissions. Livestock manure is considered to be the major source of NH_3 emission to the atmosphere (Ryden *et al.*, 1987); however, quantification of this source is difficult and comes down to estimates of loss rates, ammonia concentrations in manure and numbers of animals (refer to Appendix A). Canada has a large population of farm animals (about 114 million, mostly cattle, swine and poultry). Emission factors range from 0.32 kg NH_3 per animal per year for poultry to 40 kg NH_3 per animal per year for beef cattle (U.S. EPA, 1994). This source generated an estimated 563 000 tonnes of ammonia in 1995 (Vezina, 1997).

Manure is spread on land mainly as a way of disposing of farm animal waste. Land application of manure is higher in regions where farm animal production is high and the manure can be collected and distributed easily. In the Prairies, cattle are concentrated only in certain areas, and fields are large and require large amounts of manure for complete coverage. Although Alberta's large cattle population produces over 25% of all the animal manure in Canada (Patni, 1991), only a small proportion is confined at any time, when manure collection and land application are practical. Mixed farms and ranches are not well suited for collection and application of manure, except from cow-calf operations and feedlots. Manure in British Columbia and central and eastern Canada comes mostly from dairy and poultry farms, which are numerous and scattered throughout crop production regions. This makes it easier to get the manure to the fields where it is needed. Many dairy farms grow silage corn as cattle feed, and the manure from the cattle is applied to the cornfields, creating an on-farm nutrient cycling system.

Agricultural research shows that 10–75% of the ammonia in cattle manure can volatilize if the manure is not incorporated into the soil within a week. During hog production, 40–95% of the excreted nitrogen may be lost before the manure reaches the field. This nitrogen is lost primarily as ammonia volatilized from barns, from manure storage facilities and following field application. Many of the new hog production facilities in Canada, which include lagoon storage and slurry irrigation, will probably result in NH_3 emission losses up to 75% of the excreted nitrogen (Paul, 1997). Lockyer and Pain (1989) showed losses of up to 83% from poultry slurry, 21% from air-dried poultry manure, 36–75% from pig manure and 41% from cattle manure when applied to turf and not incorporated. In most cases, 80% or more of the ammonia loss occurred within 48 hours of application. Air-drying of poultry manure reduced ammonia losses to 12% from the poultry house and from application. Lockyer and Whitehead (1990) conducted ammonia loss experiments with cattle urine applied to soil. They found that 3.7–26.9% of the ammonia in the urine was lost within 15 days of application. Most of the loss occurred within the first 4 days. The temperature of the soil was the most important factor in determining the amount of ammonia lost to the atmosphere. They estimated average ammonia losses to air for grazing systems to be 37 kg N/ha or 12% of the ingested nitrogen content in the forage.

The quantities of ammonia lost from the soil decline considerably if the manure is liquefied and injected under the surface. Hoff *et al.* (1981) showed that liquid swine manure lost 11–14% of the ammonia when applied to the surface and only 2.5% when injected. Ryden *et al.* (1987) showed that cattle manure lost 16–32% of the ammonia when applied to the surface and only 0.9% of the ammonia when injected under the surface.

Storage systems for manure are a source of ammonia loss as well. Under acid conditions, NH_4^+, which is relatively non-volatile, predominates, while under basic conditions, NH_3, which will evaporate readily, predominates. In anaerobic decomposition of poultry manure, low-pH conditions (pH 5–6) led to a low (1%) loss of ammonia. Under aerobic decomposition, the basic pH that developed (pH 8.4–8.9) promoted loss of ammonia (9–44%). Losses of ammonia from storage tanks were reduced by up to 85% simply by covering the tanks; even a tarp sufficed (de Bode, 1990). There are many ways of handling, storing and applying manure from various animals that will reduce the loss of ammonia. The most obvious are quick storage of manure, covering manure pits to prevent volatilization, promoting anaerobic storage conditions, acidifying manure to prevent formation of NH_3 from NH_4^+, tillage of soil prior to surface application, injection of manure slurries into soil rather than surface application, and application during wet or cool weather (McGinn and Pradhan, 1997).

Mineral fertilizer application

Ammonia loss by volatilization from mineral fertilizers depends in large part on the soil pH, due to the overriding dependence of ammonia ionization on pH. NH_3 will evaporate readily, whereas NH_4^+ will not.

Some inorganic nitrogen fertilizers are acidic, so that NH_3 loss from these materials depends on soil chemical reactions or on the inherent alkalinity of the soil. Representative inorganic nitrogen fertilizers in this category are ammonium nitrate, diammonium sulphate and ammonium chloride. If the soil is sufficiently alkaline (with calcium carbonate usually), the reactions will form diammonium carbonate, which is unstable and decomposes, producing NH_3 and carbon dioxide gases (Fenn and Hossner, 1985).

The concern over nitrogen loss from industrial fertilizers has resulted in massive amounts of scientific literature on many relevant aspects. Top-applied ammonium sulphate has been measured, in both field and laboratory, to lose up to 55% of the NH_3-N. Losses from unincorporated urea can be very high, up to 60% over a period of 4 days in surface-applied pastures (Fenn and Hossner, 1985). One study by Touchton and Hargrove (1982) found that a 270 kg N/ha application of urea-ammonium nitrate to the surface resulted in less nitrogen uptake by corn than from an application of 90 kg N/ha with incorporated urea-ammonium nitrate. This equated to a loss of 67% of the NH_3-N when urea-ammonium nitrate was not incorporated.

The Environment Canada Ammonia Air Emissions Inventory for 1995 (Appendix A) estimates ammonia lost from the application of individual types of fertilizer, using appropriate emission factors and sales data. The amounts lost to the atmosphere are greatest from urea, accounting for an estimated 83% of the losses (109 232 tonnes) from applied fertilizers (Vezina, 1997). The Canadian Fertilizer Institute reported 3 million tonnes of urea produced that year (CFI, 1997), so a loss of 109 232 tonnes would be 3.6% of the total applied. This would be consistent with reported losses for incorporated urea, which is the recommended method of application.

Plant tissues

There is some evidence that plants play an important role in the concentrations of ammonia in the atmosphere. The maintenance of low ambient concentrations depends in part on the existence of an NH_3 compensation point, i.e., an atmospheric NH_3 concentration above which plants will absorb NH_3 from the air and below which they will release it. Denmead *et al.* (1977) found that, even though there was considerable release of NH_3 from the ground in a grass-clover pasture, almost none of it escaped to the atmosphere above the canopy. The effect of plant absorption was to reduce the NH_3 concentration in the air from $>16\ \mu g/m^3$ near the soil surface to $1\ \mu g/m^3$ at the top of the canopy. Other researchers report a similar phenomenon in a field of quack grass (*Agropyron repens*), reducing the NH_3 concentration from $40\ \mu g/m^3$ above the grass canopy to $3\ \mu g/m^3$ within it (Lemon and van Houtte, 1980). Accurately estimating losses from this source would be extremely difficult.

Runoff of ammonia from soil

Runoff of nutrients, including ammonia, from various land use types, including intensive livestock operations and crops, has been studied to the extent that we know the vast majority of nutrients in runoff are associated with either soluble phosphorus or nitrate. Both of these are water-soluble and easily transported in solution. Ammonia in ionized form, on the other hand, is typically tightly bound to soil colloids and is not easily transported in solution once it contacts soil. Once ammonia binds with soil, it will travel with soil particles during erosive events. Minor amounts of ammonia will travel in solution if there is freely available ammonia on the soil surface. In spring, however, considerable quantities of ammonia can be liberated as runoff from melting snow. This is due to the accumulation of ammonia trapped in snow or from deposited manure. The soil is still frozen, so that little ammonia will be absorbed and bound; what does not evaporate over winter travels with runoff and enters waterways in the freshet. Data on levels of ammonia in runoff are reported in Section 2.3.2.4.

2.3 Exposure characterization

2.3.1 Environmental fate

The nitrogen cycle is an attempt to describe the natural cycling of nitrogen from the atmosphere through incorporation into living organisms and from them back into the abiotic environment through degradative processes. Figure 1 illustrates the nitrogen cycle (after Manahan, 1994).

Several processes can create nitrogenous compounds usable by organisms from nitrogen gas (N_2). Lightning and cosmic radiation combine atmospheric nitrogen and oxygen into nitrates, which are carried to the earth's surface in precipitation. A few nitrogen-fixing bacteria, symbiotic mycorrhizal fungi living on the roots of plants, cyanobacteria, and certain lichens and epiphytes in tropical forests can split N_2 and make the nitrogen molecule available for amino acid synthesis. Ammonia is formed either as a waste product or when plants and animals die. Another set of microorganisms is capable of using NH_3 and eventually forming nitrate (NO_3^-) and nitrous oxide (N_2O).

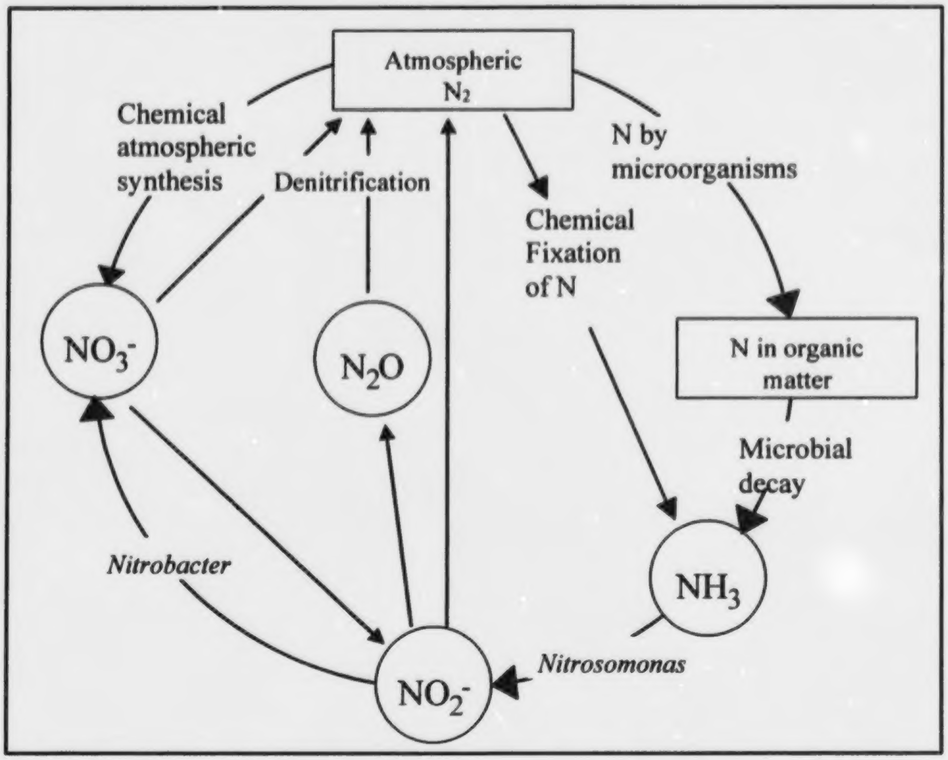
Atmospheric N2
Chemical atmospheric synthesis
Denitrification
N by microorganisms
Chemical Fixation of N
N in organic matter
Microbial decay
NO3-
N2O
NH3
NO2-
Nitrobacter
Nitrosomonas

Figure 1: The nitrogen cycle

2.3.1.1 Air

Ammonia is released into the atmosphere by agricultural, waste disposal and industrial activities. There is no known photochemical reaction by which ammonia could be produced in the atmosphere (WHO, 1986). Atmospheric ammonia undergoes four primary types of reactions: gas-phase, liquid-phase, thermal and photochemical. The first two are the most important types of reactions. From various studies consulted, the main reactions of interest appear to be those associated with the following combinations of reactants, since there is a high availability of nitric acid (HNO_3), hydrochloric acid (HCl), sulphur dioxide (SO_2) and sulphuric acid (H_2SO_4) in the atmosphere as a result of industrial and urban emissions:

- ammonia/nitric acid/ammonium nitrate ($NH_3/HNO_3/NH_4NO_3$),
- ammonia/hydrochloric acid/ammonium chloride ($NH_3/HCl/NH_4Cl$),
- ammonia/nitric acid/sulphuric acid ($NH_3/HNO_3/H_2SO_4$), and
- ammonia/sulphur dioxide (NH_3/SO_2).

In a polluted atmosphere, ammonia reacts with nitric acid and/or hydrochloric acid, which results in the formation of ammonium nitrate and/or ammonium chloride. These ammonium salts account for 10–30% of the fine aerosol (solid or liquid particles suspended in a gas with a particle diameter <0.5 μm) in a polluted atmosphere. These aerosols are very sensitive to temperature and relative humidity. In a polluted atmosphere, ammonia can also react with more than just one pollutant (Bassett and Seinfeld, 1983):

$$3NH_3\ (g) + 2HNO_3\ (g) + H_2SO_4\ (g) \Leftrightarrow (NH_4)_2SO_4{\square}2NH_4NO_3\ (s) \tag{1}$$

and

$$5NH_3\ (g) + 3HNO_3\ (g) + H_2SO_4\ (g) \Leftrightarrow (NH_4)_2SO_4{\square}3NH_4NO_3\ (s) \tag{2}$$

An intensive study (Esmen and Fergus, 1977) of the NH_3/SO_2 reaction system in a dry atmosphere led to the confirmation of at least eight reactions, the most important of which are:

$$NH_3 + SO_2 + H_2O \Leftrightarrow NH_4HSO_3 \tag{3}$$

and

$$NH_2HSO_3 + NH_3 \Leftrightarrow NH_2{\square}SO_3NH_4 \tag{4}$$

The above reactions were found to be very rapid, on the order of milliseconds. In the atmosphere, gas-phase reactions are expected to occur in the presence of water droplets. Aerosol formed through gas-phase reactions is therefore expected to act as condensation nuclei or to be captured by available drops to contribute high local concentrations of bisulphite ion (HSO_3^-). This is significant in the eventual formation of the ammonium sulphate [$(NH_4)_2SO_4$] aerosol in liquid-phase reactions. For this reason as well, reaction (3) is very important in the presence of water.

With respect to the liquid-phase reactions of the NH_3/SO_2 system, various studies (Moller and Schieferdecker, 1985; Behra *et al.*, 1989; Plass *et al.*, 1993) concluded that the function of NH_3 in this system is to neutralize the hydrogen ions formed in the absorption of sulphur dioxide and its subsequent oxidation to sulphate. Thus, NH_3 maintains sulphur dioxide solubility and the rate of sulphate production by buffering the pH to between 4 and 5.

Of all known atmospheric ammonia reactions, one of the most important seems to be that involving conversion of ammonia to ammonium (NH_4^+) particulate (see reaction 4 above). This conversion occurs in the lowest 100 m of the atmosphere at rates in the range 1×10^{-3}/s to 5×10^{-5}/s (/s is indicative of a first-order reaction, which means the reaction rate is dependent on the concentration of one reactant, namely NH_3), and daytime conversion is much faster than that at night. The reaction is dependent on temperature, relative humidity and pH (Fangmeier *et al.*, 1994).

All studies consulted conveyed the opinion that the main factors that hindered long-range transport of ammonia in the atmosphere, both vertically and horizontally, were rapid conversion to ammonium aerosol and the relatively high dry deposition velocity of ammonia.

Because of the rapid reaction rates of ammonia in air, anywhere from 56% (ECETOC, 1994) to 94% (Moller and Schieferdecker, 1985; Quinn *et al.*, 1988; ECETOC, 1994) of atmospheric ammonia is converted to ammonium particulate/ammonium aerosol. Over oceans, ammonium particulate/ammonium aerosol has an estimated atmospheric residence time of 22 hours (Quinn *et al.*, 1988); over land, the estimated residence time is in the range 7–19 days (Moller and Schieferdecker, 1985; Fangmeier *et al.*, 1994). In comparison, the estimated residence time of atmospheric NH_3 is 3.6 hours over oceans (Quinn *et al.*, 1988) and in the range of 2.8 hours to 4 days over land (Fangmeier *et al.*, 1994). These short residence times are primarily due to the rapid conversion to ammonium particulate/ammonium aerosol and the high dry deposition velocities of ammonia (Asman and Janssen, 1987; Asman *et al.*, 1989).

Figure 2 summarizes the chemistry, distribution, transport and deposition of atmospheric ammonia. Depending on the atmospheric conditions, anywhere from 56% to 94% of atmospheric ammonia is converted to ammonium particulate/ammonium aerosol, and less than 1% is converted to nitric oxide (NO). The balance remaining, 6–44%, is gaseous ammonia.

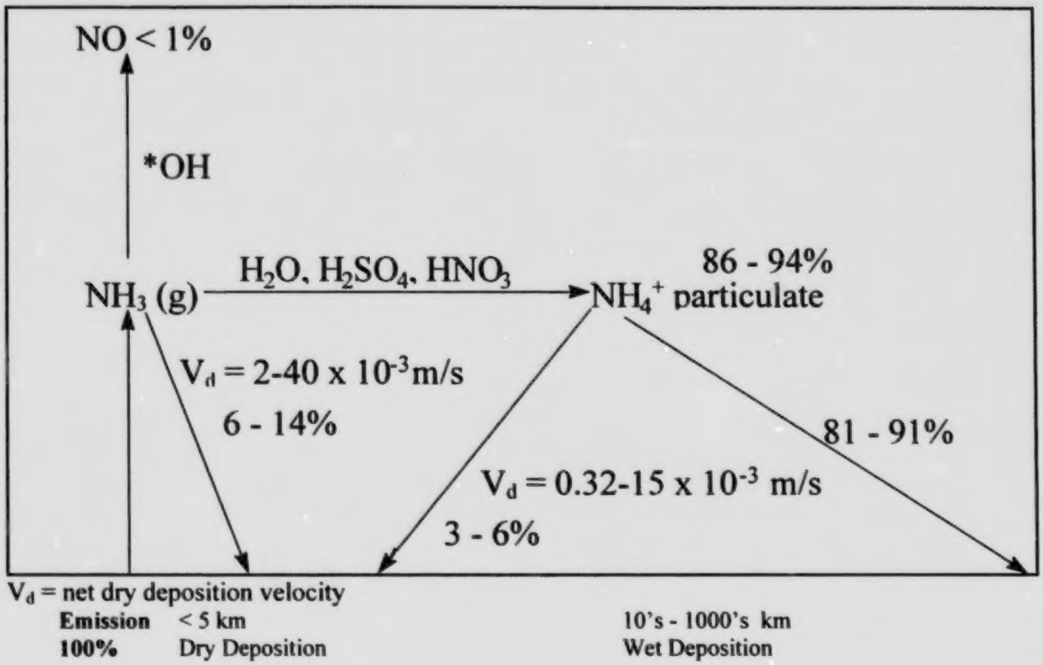
NO < 1%
*OH
NH$_3$ (g)
H$_2$O, H$_2$SO$_4$, HNO$_3$
86 - 94%
NH$_4^+$ particulate
V$_d$ = 2-40 x 10^{-3}m/s
6 - 14%
81 - 91%
V$_d$ = 0.32-15 x 10^{-3} m/s
3 - 6%
V$_d$ = net dry deposition velocity
Emission
100%
< 5 km
Dry Deposition
10's - 1000's km
Wet Deposition

Figure 2: Fate analysis of ammonia in the atmosphere

It is known from measurements that gaseous ammonia concentration rapidly decreases with height and distance from ground-level emission sources. Results of four studies on the decrease in ammonia concentration with an increase in distance from a ground-level emission source showed that 50–75% of the gaseous ammonia detected was deposited between 500 and 4000 m from the source (Denmead *et al.*, 1982; Asman *et al.*, 1989; Fangmeier *et al.*, 1994; Janzen *et al.*, 1997).

Gaseous ammonia is removed from the atmosphere via dry deposition, whereas ammonium aerosol is removed via both dry and wet deposition. Dry deposition is most significant in regions with high ammonia emissions and is indicative of short-range transport of less than about 5 km. In contrast, wet deposition is most significant in regions with low ammonia emissions and is indicative of long-range transport, ranging from tens to thousands of kilometres distant (ECETOC, 1994; Fangmeier *et al.*, 1994).

Ammonia may be a significant local pollutant and, as a precursor of nitric oxide and ammonium aerosols, can have long-range impacts.

2.3.1.2 Surface water

A fate analysis for ammonia in the aquatic environment is displayed schematically in Figure 3 and is a composite from several reviews (NRC, 1979; API, 1981; WHO, 1986). Ammonia has a critical role in the nitrogen cycle, so that when it is introduced into aquatic systems, it is usually rapidly transformed into other nitrogenous forms (e.g., nitrates and organically bound nitrogen).

The major processes include fixation, assimilation, ammonification, nitrification and denitrification. In the sections below, these major processes are discussed along with reference to decreases in ammonia concentration due to dilution.

Figure 3 also presents the relative importance of input sources and depletion routes for ammonia in the aquatic environment. Nitrification and volatilization are the important and competitive fate processes in surface waters that are not ice covered. Under ice cover, both processes are greatly reduced. Volatilization is the predominant removal process for industrial effluents until the effluents are diluted to a concentration that is not harmful to nitrifying bacteria. These bacteria require a substrate on which to grow, typically suspended solids in the water. Nitrification processes are more likely to be significant in lakes, slow-moving rivers, estuaries and sewage effluents. Nitrification is important in preventing the persistence or accumulation of high ammonia levels in water receiving sewage effluent or runoff. However, winter conditions will inhibit bacterial growth so that under restricted water flow conditions, ammonia can build up in receiving waters. Conditions of high nitrification may contribute to low levels of dissolved oxygen, as nitrification is an oxygen-consuming process (WHO, 1986).

Nitrification of ammonia can also have significant impacts on water systems by promoting acidification. In a greenhouse, seven identical mini-ecosystems, simulating soft-water ponds, were exposed to different types of artificial rainwater. Although ammonium sulphate deposition was only slightly acidic, due to nitrification it acted as an important acid source, causing acidification to pH 3.8. Under acidified conditions, ammonium sulphate deposition led to a luxuriant growth of *Juncus bulbosus* and *Agrostis canina*. In the mini-ecosystems, sulphuric acid deposition with a pH of 3.5 decreased the pH of the water to only 5.1 within 1 year (Schuurkes *et al.*, 1986).

Loss of ammonia to the atmosphere at elevated pH is another mechanism for ammonia removal. It has been estimated (API, 1981) that volatilization could account for 67.5% of the observed loss of ammonia below an industrial discharge to the Wabash River in the United States. It was also estimated that 20% of the ammonia discharged by a fertilizer plant was lost to the atmosphere, and a 55% loss for 10-year, 7-day low-flow conditions was predicted.

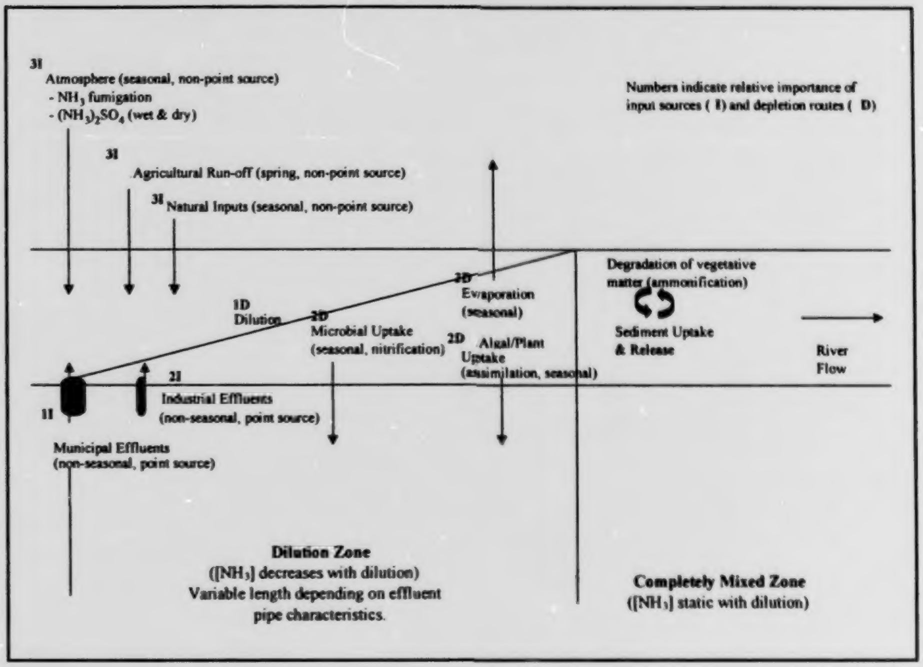
3I
Atmosphere (seasonal, non-point source)
- NH_3 fumigation
- $(NH_3)_2SO_4$ (wet & dry)
Numbers indicate relative importance of input sources (I) and depletion routes (D)
3I
Agricultural Run-off (spring, non-point source)
3I Natural Inputs (seasonal, non-point source)
2D
Evaporation (seasonal)
Degradation of vegetative matter (ammonification)
1D
Dilution
2D
Microbial Uptake (seasonal, nitrification)
2D Algal/Plant Uptake (assimilation, seasonal)
Sediment Uptake & Release
River Flow
2I
Industrial Effluents (non-seasonal, point source)
1I
Municipal Effluents (non-seasonal, point source)
Dilution Zone
([NH_3] decreases with dilution)
Variable length depending on effluent pipe characteristics.
Completely Mixed Zone
([NH_3] static with dilution)

Figure 3: Fate analysis of ammonia in aquatic environments

2.3.1.3 Soil and groundwater

A schematic of the terrestrial nitrogen cycle is represented in Figure 1. Ammonium is an important intermediate in the assimilation of nitrogen from the soil by plants. Nitrogen is present in the soil largely in the organic form and is unavailable to plants. Microbial processes must mineralize it. As nitrification is an energy-yielding process, the rates of conversion are rapid, so that ammonium rarely accumulates in soil while bacteria are active. Organic nitrogen compounds are reduced to ammonium, which is converted to nitrite (NO_2^-) by *Nitrosomonas* and then to nitrate by *Nitrobacter* (API, 1981; WHO, 1986). Most plants can assimilate the ammonium ion, but it is usually oxidized to the nitrate ion, the most common form of mineralized nitrogen in soil, which may be assimilated by plants as well (NRC, 1979; WHO, 1986).

Another source of mineralized nitrogen is nitrogen fixation, where gaseous nitrogen is transformed to ammonium ion, usually by metabolic processes. Nitrogen fixation occurs in blue-green algae and a few genera of microorganisms, which include aerobic bacteria, such as *Azotobacter* species, anaerobic bacteria, such as *Clostridium* species, and organisms in symbiotic association with higher plants, such as *Rhizobium* species found in legumes. Volatilization, adsorption and chemical transformation will also affect the fate of ammonia in soil (NRC, 1979; WHO, 1986).

Ammonia is bound in soil by the attraction of the positive charge on the ammonium ion to the negatively charged soil micelles. In soil, ammonium is adsorbed primarily by four mechanisms: chemical (exchangeable), fixation (non-exchangeable), reaction with organic matter and physical attractive forces.

Since ammonia is so poorly mobile in soil, it is unlikely to leach to groundwater except under unusual circumstances, such as when the cation exchange capacity of the soil is exceeded. The worst situation for ammonium leaching would probably occur when the soil is at field capacity with respect to water. In this case, ammonium ions can penetrate the soil and continue downward, with only small amounts remaining as part of the interstitial fluid. Moisture that is present in the soil or added as precipitation will dilute ammonia on the surface and reduce its rate of evaporation.

If ammonium ions reach the groundwater table, they will continue to move in the direction of groundwater flow and will be diluted slowly through diffusion or will be adsorbed by soil and mineral particles. It is possible that deep-soil bacteria utilize ammonia for amino acid synthesis in the presence of oxygen.

2.3.2 Environmental concentrations

2.3.2.1 Air

Atmospheric levels of gaseous ammonia in urban areas around the world are on average about 20 $\mu g/m^3$. Japanese researchers found ammonia concentrations up to 210 $\mu g/m^3$ downwind of a heavily industrialized area of Tokyo. Non-urban sites can have a wide range of levels (0.2–2000 $\mu g/m^3$), depending on their proximity to point sources (WHO, 1986). One such area in California was studied as a comparison with urban areas. Air near a large 600-animal dairy farm had an ammonia concentration of 560 $\mu g/m^3$ (Luebs *et al.*, 1973), and air in the region contained 190 $\mu g/m^3$ on a routine basis. Concentrations of ammonia in the troposphere are heavily influenced by ground temperature and so exhibit strong seasonal variations. German researchers found winter concentrations of 1–2 $\mu g/m^3$ at 1500 m in winter and 5 $\mu g/m^3$ at 4000 m in summer (WHO, 1986). Levels of particulate NH_4^+ ions in the atmosphere above the oceans have been studied; concentrations were found to be between 0.01 and 0.12 $\mu g/m^3$ (Servant and Delapart, 1983; Quinn *et al.*, 1988). The authors concluded that the oceans are a source of ammonia for the atmosphere. The general background concentration of ammonium in particulates is around 1 $\mu g/m^3$, with a measured average for an American urban area of 7.6 $\mu g/m^3$. In general, atmospheric ammonia levels show a seasonal variation, with the lowest levels occurring during the summer and the highest during the winter in Europe, and a reversed pattern in Japan (WHO, 1986; Yamamoto *et al.*, 1995). For the 1970s, rainfall in the continental United States had concentrations of ammonia ranging from 0.01 to 0.15 mg/L (NRC, 1979). In a mixed coniferous stand at Whitaker Forest in the western Sierra Nevada Mountains, California (1988–1990), seasonal ammonia 12-hour daytime averages of 1.11–1.56 $\mu g/m^3$ were recorded, with the highest 12-hour daily averages reaching 3.75 $\mu g/m^3$. When expressed on a molar basis, NH_3 was the most abundant nitrogen air pollutant and represented almost 50% of the total nitrogen (Bytnerowicz and Riechers, 1995). In Edmonton, Alberta, the average concentration in rainfall was 0.41 mg NH_4^+/L during the summers of 1977 and 1978. In July 1978, an intensive sampling effort detected a distinct gradient of total ammonia, with low values (<0.06 mg/L) found in the foothills of the Rocky Mountains and high values (>0.4 mg/L) eastwards into the agricultural areas of the province (Klemm and Gray, 1982).

Table 3 provides some atmospheric concentrations of ammonia and ammonium from regions with different sources. There is considerable variation in atmospheric concentrations of total ammonia, even in unpolluted regions; however, agriculturally polluted regions, particularly in Europe and California, can have very high concentrations (up to 4000 µg/m^3).

Table 3: Atmospheric ammonia and ammonium aerosol concentrations at various locations

Location	NH_3 (µg/m^3)	NH_4^+ (µg/m^3)	Reference
Urban regions			
Uniontown, Pennsylvania	5		Suh *et al.*, 1992
University of Essex, England	33	51	Li and Harrison, 1990
Industrially polluted regions			
Windsor, Ontario	1.6–7.6		Brook *et al.*, 1997
Hamilton, Ontario	3–43.6		Brook *et al.*, 1997
Site near Nanticoke coal-fired power plant on Lake Erie, Ontario	75	50	Anlauf *et al.*, 1985
Yokohama, Japan	41–202		Yamamoto *et al.*, 1995
Agriculturally polluted regions			
Riverside, California	68–1734	486–2000	Doyle *et al.*, 1979
Semi-rural area in the Netherlands	12–661	0–295	Hoek *et al.*, 1996
Rural area in the Netherlands	12–980	5–373	Hoek *et al.*, 1996
Agricultural area in the Netherlands	272–544		Asman *et al.*, 1989
Egbert, Ontario	1.3–9.3		Brook *et al.*, 1997
Southeastern Saskatchewan	85		Cheng and Angle, 1996
Unpolluted regions			
Emission-free moorland in the Netherlands		37	Asman *et al.*, 1989
West coast of Canada	17		Cheng and Angle, 1996
Sutton, Ontario	0.8–4.2		Brook *et al.*, 1997
Kejimkujik National Park, Nova Scotia	0.3–9.4		Brook *et al.*, 1997
Hungary	12	23	Fekete and Gyenes, 1993
Antarctica	0.2–0.5	0.2–0.9	Gras, 1983
Southwest coast of Europe	2–8	1.7–28	Pio *et al.*, 1996

At the Hubbard Brook Experimental Watershed in New Hampshire, Fisher *et al.* (1968) detected 0.18–0.22 mg NH_4^+/L for the years 1965–1968.

Janzen *et al.* (1997) collected precipitation around Lethbridge, Alberta, and analysed it for ammonia and nitrate in an attempt to determine the nitrogen cycling in local soils. Analysis of precipitation collected over a 2-year period suggested that the annual nitrogen input, as nitrate and ammonium, amounted to 5.6 kg N/ha. The authors cited Peake and Wong (1992) to provide an average ratio of 19 μeq NH_4^+ to 14 μeq NO_3^- for rainfall around Lethbridge. Using this ratio with a mean total nitrogen input of 5.6 kg N/ha gives a mean annual input of 3.2 kg NH_3/ha.

The Canadian Acid Aerosol Measurement Program was established to gain an understanding of the atmospheric behaviour of particulate acidity, which involved the measurement of gaseous ammonia (Brook *et al.*, 1997). The mean concentrations are assumed to be representative of typical ammonia levels in the early to mid-1990s. Mean concentrations of 1.72 and 4.28 mg/m^3 were observed at sites with industrialization and human populations (Windsor and Hamilton, Ontario, respectively). Intense agricultural activity also produced elevated mean concentrations of 1.63 mg/m^3 (Egbert, Ontario). In non-industrialized rural settings, mean concentrations were lower, at 0.83 mg/m^3 (Sutton, Quebec); over water, concentrations were 0.41 mg/m^3 (Kejimkujik National Park, Nova Scotia).

2.3.2.2 Atmospheric deposition

Researchers at the Lethbridge Agricultural Research Station (Janzen *et al.*, 1997) measured the rate of NH_3 deposition to soil at nine sites throughout southern Alberta for up to 2 years. Lowest average rates, typically about 4–6 kg N/ha per year, were observed at the two control sites at the Research Station, while the highest average rates (about 66 kg N/ha per year) were observed near a beef feedlot. The high rates are enough to significantly affect soil nitrogen fertility. The researchers also studied the relationship between distance from NH_3 source and the rate of NH_3 deposition. Soil collectors were set up at various distances downwind of the feedlot; deposition rates were highest close to the feedlot and then diminished with distance. Average background deposition rates (4.4 mg N/m^2 per day) were not reached within 1 km (Figure 4).

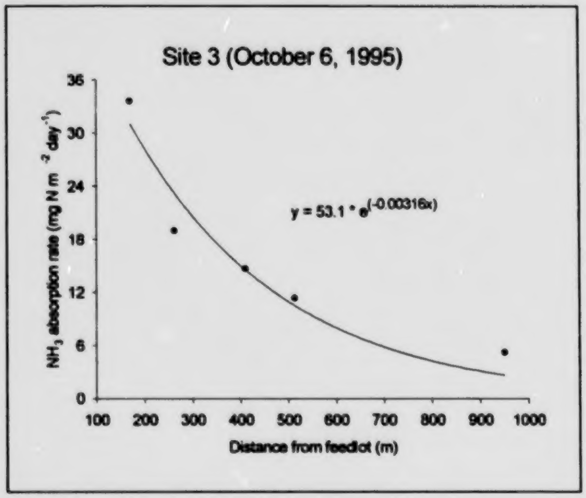

Figure 4: Dispersion of NH_3 downwind of a feedlot

This is similar to atmospheric dispersion of ammonia from other areas of the world where intensive livestock facilities exist. The air above a large dairy area in Chino, California, and from an area not close to known ammonia sources was sampled for ammonia. The livestock area was 150 km^2 containing 143 000 dairy cows on 380 dairies (Luebs *et al.*, 1973). Continuous simultaneous sampling of the air at the dairy area site and at the control site showed the nitrogen concentration to be 23 times greater within the dairy area, with concentrations of 80 μg/m^3 at the dairy area site compared with 3–5 μg/m^3 at the control site. Rainfall measurements showed that the rain over the dairy area contained roughly 3 times more distillable nitrogen than the control area. The ammonia concentrations ranged from 0.4 to 1.7 mg/L in the dairy area compared with a range from 0.2 to 0.6 mg/L in the control area. The rainfall in the dairy area added 1.59 kg N/ha to soils compared with 0.53 kg N/ha in the control area. At the fence line of the dairy area, concentrations of distillable nitrogen were 540 μg/m^3; at 200 m, NH_3 concentrations were roughly 50 μg/m^3; and at 800 m downwind, the concentrations were 18 μg/m^3 (Luebs *et al.*, 1973).

In one U.S. study, a lake 2 km from a large cattle feedlot (90 000 head of cattle) was found to receive considerable quantities of ammonia from the air, sufficient to raise its total nitrogen concentration by 0.6 mg/L over a year. On average, the differences in atmospheric concentrations of NH_3 between background sites and those closest to the feedlot (400 m) were 20-fold. The average deposition of ammonia closest to the feedlot was 145.6 kg NH_3/ha per year, while at the background site it was 7.8 kg/ha per year (Hutchinson and Viets, 1969).

Ammonia flux density was determined above a large feedlot to be on average 1.4 ± 0.7 kg N/ha per hour in spring and summer in northeast Colorado. A feedlot surface had lower average values than this when wet, but higher values than this during drying. Total NH_3 emissions equalled about half the rate of urinary nitrogen deposition, or about one-quarter of the rate of total nitrogen deposition (Hutchinson *et al.*, 1982). Actual ammonia concentrations were fairly stable, being 361 ± 46 μg NH_3-N/m^3. Drying events and periods of warm, calm weather generated much higher NH_3 concentrations (970–1200 μg NH_3-N/m^3).

Deposition of up to 66.4 kg NH_3/ha per year was determined within 50 m of a poultry house containing 8000–12 000 chickens near Athens, Georgia. At 1.2 km from the poultry house, the ammonia trapped was at background deposition rates (15 kg/ha per year). Near a beef cattle feedlot, 26.5 kg/ha per year was trapped. At distances greater than 500–800 m, the concentrations dropped to background for the Athens area (Giddens, 1975).

Nitrogenous air pollutants were monitored during three summer seasons (1988–1990) in a mixed coniferous stand at Whitaker Forest in the western Sierra Nevada Mountains, California. NH_4^+ deposition fluxes to ponderosa pine (*Pinus ponderosa* Dougl. ex Laws.) branches during the three summer seasons ranged from 17 to 67 kg/m^2 per year. During the 1990 summer season, NH_4^+ washed from branch surfaces provided 0.2 kg/ha per year. The estimated internal uptake of NH_3 was 0.6 kg N/ha per year. The elevated levels of air pollutants and nitrogen deposition could adversely affect the natural ecosystems of the western Sierra Nevadas (Bytnerowicz and Riechers, 1995).

Total inorganic nitrogen deposition in the most highly exposed forests in the Los Angeles Air Basin may be as high as 25–45 kg/ha per year. Nitrogen deposition in these highly exposed areas has led to nitrogen saturation of chaparral and mixed conifer stands. In nitrogen-saturated forests, high concentrations of nitrate are found in stream water, soil solution and foliage (Bytnerowicz and Fenn, 1996).

2.3.2.2.1 Case study: The Lower Fraser Valley

In the Lower Fraser Valley, deterioration of surface water, groundwater and air quality is a major environmental issue. There is particular concern about the potential for nitrate pollution of the Abbotsford/Sumas aquifer, which supplies both Canadian and U.S. drinking water in the area (Zebarth *et al.*, 1997), as well as a decline in the visible air quality around Vancouver (Hoff *et al.*, 1997; Pryor *et al.*, 1997a,b,c). The source of the nitrates is manure applied to fields in winter, and the cause of the reduced air quality is ammonium sulphate particulates. The valley has many farms and livestock facilities that contribute to both direct volatilization of NH_3 and local redeposition (Paul, 1997).

In order to conduct an ammonia modelling project, an NH_3 air emissions inventory was constructed using the latest census data available (1996) from both Canadian and U.S. sources (Jennejohn *et al.*, 1996; Barthelmie and Pryor, 1998). The ammonia emissions inventory for the Lower Fraser Valley in 1996–1997 is shown in Figure 5. Agriculture dominates NH_3 emissions in the Lower Fraser Valley, with an estimated generation of 5260 tonnes/year, while the Greater Vancouver Regional District generates 3511 tonnes/year. Cattle contribute approximately half of the agricultural NH_3 emissions, poultry are the next major source and mineral fertilizer use contributes significantly (Barthelmie and Pryor, 1998). Approximately 8800 tonnes of ammonia come from the Canadian part of the valley and 2400 tonnes from the U.S. portion.

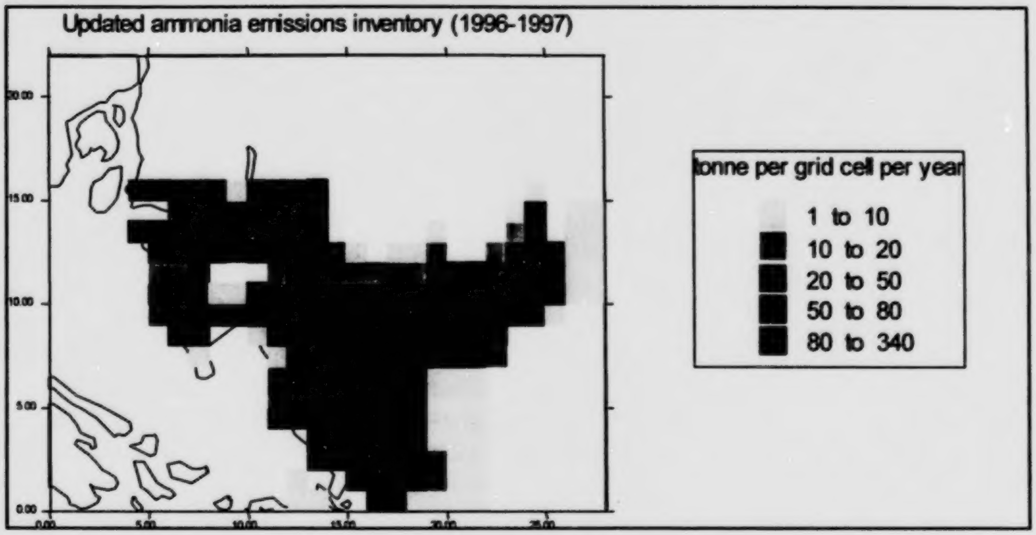

Figure 5: Ammonia air emissions inventory for the Lower Fraser Valley, 1996–1997

Since ammonia is chemically important to the production of atmospheric aerosols, understanding the concentrations and deposition of ammonia requires modelling the atmospheric chemistry of aerosols. The Inorganic and Secondary Organic Particle (ISOPART) model was used because it is a Lagrangian model with extensive chemistry and aerosol dynamics.

Atmospheric sampling relevant to the current application was undertaken (Hoff *et al.*, 1997). In addition to airborne monitoring, intensive ground-based sampling took place in the summer of 1993 during the Regional Visibility Experimental Assessment in the Lower Fraser Valley (REVEAL) campaign. Aerosol samplers were deployed at seven locations in the Fraser Valley to collect 24-hour averaged fine particulate and gas concentrations (Pryor *et al.*, 1997a,c).

A comparison of modelled near-surface and surface observed aerosol concentrations was performed for the afternoon of August 5, 1993. The areas of highest aerosol concentrations were observed east of Vancouver in the north-central valley in a band running from northwest to southeast. This pattern of aerosol concentrations was also predicted by ISOPART for this period (Pryor *et al.*, 1997b), giving confidence to the aerosol components of the model such that gaseous ammonia concentrations can be derived.

As expected, for NH_3, the highest concentrations were in the central and eastern portions of the valley, in mainly agricultural areas (the source region); the urban area of Vancouver is a source of NO_y (total nitrogen oxide compounds, including nitrate). Ammonium aerosol concentrations were high in a band from Greater Vancouver southeast towards the central valley, while nitrate concentrations were highest around Vancouver and in the central valley. It should be noted that the peak in NH_4^+ concentrations was associated with high sulphate concentrations.

Figure 6 shows total modelled nitrogen deposition in kg N/ha per year. For NH_3, the highest deposition is over the central and eastern portions of the valley, shown as the concentration area on the right side of the figure (labelled NH_3); this is the source region for ammonia. NO_y deposition is primarily in Greater Vancouver and the highly urban portions of the domain, shown as the concentration area on the left side (labelled NO_3^-). Ammonium aerosol deposition is highest in a band from Greater Vancouver southeast towards the central valley, while nitrate deposition is highest east of Vancouver and over the downtown region. This pattern of nitrogen deposition is to be expected, as it represents two major and separate source regions. Ammonia is rapidly redeposited as a gas, but it is also relatively rapidly converted to the aerosol phase and both transported and deposited as NH_4^+. Estimated maximal ammonia deposition was 105 kg NH_3/ha per year in the rural portions of the Lower Fraser Valley. Most of the agricultural portion of the valley is subjected to a level of nitrogen deposition (primarily as ammonia) considerably greater than the critical load of 10 kg/ha per year (Figure 6). The grid numbers in Figure 6 correspond to the grid numbers in Figure 5.

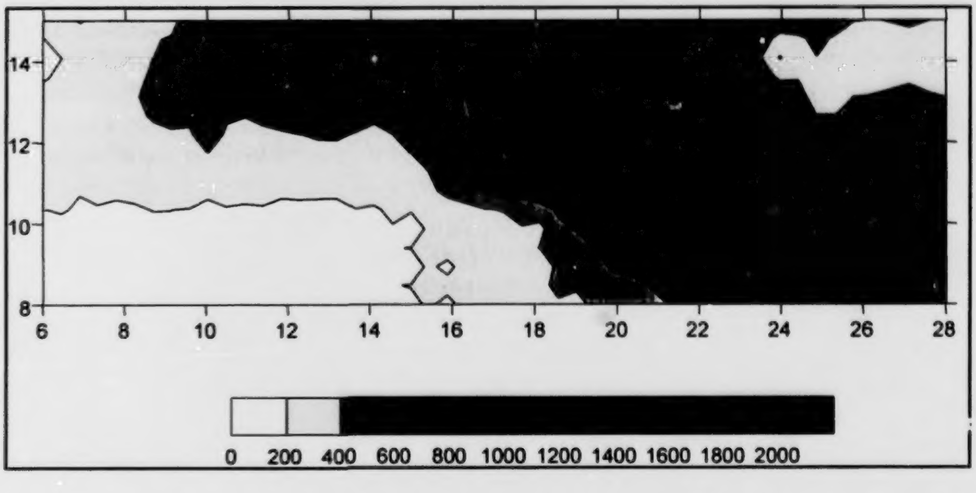

Figure 6: Modelled total nitrogen deposition (kg/ha per year) for the Lower Fraser Valley

2.3.2.3 Surface water

Natural waters typically contain little total ammonia, usually in concentrations below 0.1 mg/L. Assuming temperatures of 20°C (typical of times when risk is highest and which are the focus of the risk scenarios) and pHs in the 7–8 range, natural NH_3 levels are in the 0.0004–0.004 mg/L range. Higher concentrations may be an indication of anthropogenic input and organic pollution (CCREM, 1987). This tendency is shown in Figure 7 for waters above and below Edmonton. Above Edmonton, un-ionized ammonia was almost non-detectable (based on the detection limit for total ammonia); at 113 km downstream, un-ionized ammonia ranged as high as 0.026 mg/L and was consistently detected (Tchir, 1998). The highest concentration of un-ionized ammonia in Canadian municipal effluents was 0.68 mg/L, detected in effluents from the Annacis Island facility, Vancouver (Servizi *et al.*, 1978).

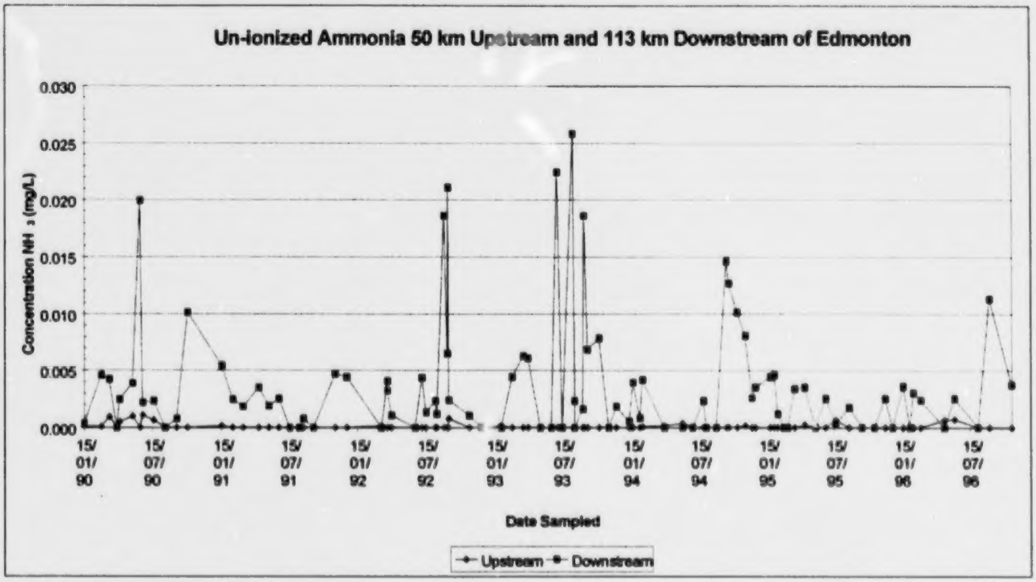

Figure 7: Un-ionized ammonia concentrations upstream and downstream of Edmonton

Data on ammonia concentrations in fresh waters were collected from federal and provincial monitoring agencies and were examined in order to identify hot spots. Detection limits for un-ionized ammonia must be calculated from the detection limit for total ammonia at a specific pH and temperature. As these two parameters change, the detection limit for un-ionized ammonia will fluctuate; therefore, non-detectable limits for un-ionized ammonia are simply noted as "<detectable." A general analysis of water quality was received from the Ontario Ministry of Environment and Energy (OMEE, 1997). The average un-ionized ammonia concentration was 0.007 mg/L, with a median value of 0.0004 mg/L and range of <detectable–5.6 mg/L.

Only total ammonia concentrations were reported from across British Columbia (Ryan, 1998; Swain, 1998). They were generally very low, indicating perhaps the large dilution capacity of the rivers and lakes in the province. For the federal government monitoring sites, the average total ammonia concentration was 0.009 mg/L, with a median of 0.005 mg/L and a range of <0.002–0.48 mg/L. From the provincial monitoring sites, the average total ammonia concentration was 0.02 mg/L, with a median of 0.001 mg/L and a range of <0.002–8.4 mg/L.

The Northwest Territories and Nunavut also had extremely low ammonia concentrations in rivers, as would be expected for those territories. The average total ammonia concentration was 0.03 mg/L, with a median of 0.01 mg/L and a range of <0.002–0.68 mg/L (Halliwell, 1998).

There were 1225 samples from 66 sites for the three Prairie provinces from Environment Canada, primarily from interprovincial river sites in 1994 and 1995. Ammonia, temperature and pH measurements were taken so that un-ionized ammonia concentrations could be calculated

(Chu, 1997). The average un-ionized ammonia concentration was 0.002 mg/L, with a median of 0.0006 mg/L and a range of <detectable–0.16 mg/L.

Alberta Environmental Protection provided detailed sampling data, but no temperature or pH values (Tchir, 1998). Many of the Alberta data indicated that cities and major industrial centres are elevating ammonia concentrations in the province's streams. The average total ammonia concentration was 0.8 mg/L, with a median of 0.02 mg/L and a range of <0.002–126 mg/L.

Manitoba Department of the Environment has taken water samples from 44 sites. The average un-ionized ammonia concentration was 0.002 mg/L, with a median of 0.0004 mg/L and a range of <detectable–0.21 mg/L (Williamson, 1998).

The City of Winnipeg supplied water quality monitoring data that it collects below each of its sewage treatment plants and downstream of Winnipeg at Lockport Dam (Ross, 1998). At the Fort Garry Bridge below the South End facility, the average un-ionized ammonia concentration was 0.012 mg/L; the median was 0.006 mg/L, with a range of <detectable–0.13 mg/L. At the Main Street Bridge, where the Assiniboine River joins the Red River, the average un-ionized ammonia concentration was 0.006 mg/L, the median was 0.003 mg/L and the range was <detectable–0.04 mg/L. At the North Perimeter Bridge on the Red River, the average un-ionized ammonia concentration was 0.017 mg/L; the median was 0.007 mg/L, with a range of <detectable–0.17 mg/L. At the Lockport Dam on the Red River, the average un-ionized ammonia concentration was 0.017 mg/L, the median was 0.01 mg/L and the range was <detectable–0.14 mg/L.

Two concentrations are available from the Lake Ontario sampling surveys done in 1992 and 1993. One is 0.96 mg/L, measured in Hamilton Harbour in 1992, and the other is 0.39 mg/L, measured in an area of east Toronto known as The Beaches, also taken in 1992 (Charlton, 1997).

Water from the centre of Hamilton Harbour has been analysed for ammonia since at least 1986; the results show routinely high concentrations of total ammonia, which builds up in the winter and degrades throughout the summer. This ammonia concentration process is the result of three municipal WWTPs depositing their effluents in the harbour, reduced water exchange in the harbour and the reduction in nitrifying bacteria in the winter. Environment Canada undertook a weekly survey in 1998 (January 6 – September 9) to determine the extent of ammonia concentrations throughout the harbour (Charlton and Milne, 1999). At 1 m depth, the average un-ionized ammonia concentration was 0.023 mg/L; the median was 0.016 mg/L, with a range of 0.001–0.114 mg/L. These values all declined through the water column, so that at 19 m depth the average was 0.004 mg/L, with a median of 0.003 mg/L and a range of <detectable–0.012 mg/L.

The province of Quebec provided water quality data, including total ammonia, temperature and pH, for the years 1988–1998 (Dupont, 1998). Based on data for 16 372 samples, the average un-ionized ammonia concentration was 0.001 mg/L, the median was less than a detectable concentration (based on a total ammonia detectable limit of 0.002 mg/L) and the range was <detectable–0.69 mg/L. Many streams and rivers on the south shore of the St. Lawrence River have very high pH values in summer; this, combined with high summer temperatures,

generates high un-ionized ammonia concentrations, even when there are relatively low concentrations of total ammonia. It appears that many of the streams with high average total ammonia concentrations are just north or south of Montréal or east of the Québec area on the south shore.

2.3.2.4 Soil runoff

Timmons and Holt (1977) determined the quantities and chemical composition of runoff from native (undisturbed by humans) prairie soils in Minnesota. Over 5 years, they determined that runoff from snowmelt accounted for 80% of the average annual ammonia in runoff. Rainfall caused appreciable runoff only in 1 year (37%). Dissolved ammonia losses ranged from 0.02 to 0.28 kg NH_3-N/ha in snowmelt, with rainfall-derived runoff containing 0.03 kg/ha in that year. The average loss of ammonia from native land was 0.13 kg/ha.

In a controlled deforestation study, Likens *et al.* (1970) showed that complete deforestation of a watershed in the eastern forests of New Hampshire had no effect on the runoff of ammonium. In watersheds that were not cut, the concentration of ammonium over 3 years in runoff ranged from 0.02 to 0.12 mg/L; in the cut watershed, the concentration of ammonium in the runoff ranged from 0.05 to 0.14 mg/L.

Data from 32 forested stream catchments in the Muskoka-Haliburton area of central Ontario, collected over 8 years, were used to develop regression models of long-term NH_4^+ export. There was a weak correlation between stream chemistry (including NH_4^+) and discharge for any site. Retention (defined as the fraction of annual deposition retained by the catchment) was very high (>0.87) for ammonium in all catchments. Deposition of NH_4^+ for the area was 4.794 kg NH_4^+/ha per year (Dillon *et al.*, 1991).

Animal husbandry can significantly elevate the runoff of ammonia from land. Cooke (1996) studied the variations in nitrogen runoff from various land types in Alberta. Under forested land, neither nitrate nor NH_4^+ concentration was high in surface runoff. Under cropland, nitrate dominated, its concentration approaching 50 times the NH_4^+ concentration. Under agricultural land with cattle grazing (25–100 head), runoff delivered 95% of NH_4^+ to streams. Only 2% of the nitrogen in cropland streams was ammonia, 43% of nitrogen in forest streams was ammonia and 89% of nitrogen in streams draining cattle operations was ammonia.

Peak NH_4^+ concentrations were 27 mg/L below cow-calf operations, while spring concentrations in the forested streams were below 1 mg/L. Flow-weighted mean concentrations of 1–2.3 mg/L for NH_4^+ and 0.15–0.2 mg/L for nitrate were detected below cow-calf operations in the spring.

A provincial stream survey in Alberta found that nutrient concentrations tend to be higher in streams that drain intensively farmed land than in streams that drain less intensively farmed land. Typical seasonal patterns were apparent: 1) highest concentrations were generally measured during spring runoff, 2) concentrations declined as flows subsided, and 3) later in spring and in summer, increases in nutrient levels (especially particulates) usually coincided with sudden increases in rainfall. These sudden concentration increases were more apparent in streams that drain land farmed with medium and low intensity, because rain-induced runoff occurred in these drainage basins, whereas none occurred in basins with high agricultural intensity (Anderson *et al.*, 1998b).

Application of manure to fields can be a cost-effective means of disposal of animal wastes and a cost-effective fertilizer; however, at some times of the year, application can be problematic for nearby watercourses. In Quebec, Gangbazo *et al.* (1995) determined that fall application of manure, as a fertilizer, created significant quantities of ammonia in runoff. The fall application of 360 kg manure-N/ha to corn increased ammonia in runoff from 1.9 to 3.4 kg N/ha. The runoff concentrations were elevated for at least 3 years. For surface application to forage, only the fall application of 110 kg manure-N/ha caused excessive ammonia in field runoff. Ammonia was elevated for 2 years over controls.

In Manitoba, Green (1996) studied the spring runoff of ammonia from hog manure surface-applied in the winter. Mean ammonia concentrations were considerably higher in runoff than in field pools. Meltwater from control fields contained 0.19–0.26 mg ammonia/L, while that from manured fields contained 8.5 mg/L. Concentrations of total ammonia in local rivers were relatively high, both upstream (0.32 mg/L) and downstream (0.34–0.52 mg/L) of the study site. There was no apparent impact on local watercourses from the application, despite the fact that substantial quantities of ammonia were leaving the site in runoff.

As part of a eutrophication study in Iowa, Jones *et al.* (1976) made detailed measurements of the concentrations of nutrients in runoff from 48 small and large watersheds. They also conducted an inventory of the animal densities in the watersheds, the types of animal holding facilities in each and the land use in each watershed. In watersheds of over 100 ha, ammonia in stream water was significantly correlated only with the animal units/ha in the watershed. The researchers determined that NH_3-N was increased by 0.77 ± 0.23 mg/L for each animal unit/ha within the watershed. They also determined whether animal placement within the watersheds influenced NH_3-N losses. The number of feedlot animal units/ha with drainage to streams or tile intakes was the only significant variable in the analyses. Jones *et al.* (1976) estimated that 0.96 ± 0.18 kg NH_3-N/ha were associated with each feedlot animal unit/ha with drainage to streams or tile intakes. Concentrations of ammonia in feedlot runoff averaged 6.5 mg/L, while runoff from soybean fields, cornfields and pastures was in the 0.75–1.0 mg/L range. There was no ammonia detected in tile runoff from fields.

Intensive dairy operations conducted in close proximity to streams have the potential to contaminate local watercourses with high levels of ammonia, especially if they have steep slopes to drainage. Daniel *et al.* (1982) showed this with a survey of three dairies in Wisconsin and an urban construction site. The runoff from an intensive dairy operation on a steep slope and in close proximity to a stream contained 5 mg ammonia/L, while runoff from dairies either far removed from streams or on flat land contained around 1 mg ammonia/L. Runoff from the construction site contained around 0.2 mg/L.

2.3.2.5 Soil

There are few data on naturally occurring concentrations of ammonia in Canadian soils. In general, natural ammonia levels in soil are very low (<1 mg/kg) due to the rapid conversion of ammonium to nitrite by *Nitrosomonas* species and then to nitrate by *Nitrobacter* species in the temperature range 0–35°C (Henry, 1995). In some areas of Canada, such as the Lower Fraser Valley, conditions may exist in winter where ammonia can build up in soil due to the application of manure to fields that are not frozen but are too cold for *Nitrosomonas* species to grow.

2.3.2.6 Groundwater

There are few data on concentrations of ammonia in Canadian groundwater. Ammonia contamination of groundwater is not usually an issue, as it is readily converted to positively charged ammonium ions that bind tightly to negatively charged cation exchange sites in soil. Ammonium is not sufficiently mobile in soil to create widespread groundwater contamination problems (Feth, 1966; Liebhardt *et al.*, 1979; Olson, 1997). In rare instances, nitrogen fertilizers, livestock wastes and septic tanks may contribute significant amounts of ammonia to shallow groundwater, especially those underlying poorly drained soils (Gilliam *et al.*, 1974; Rajagopal, 1978), those underlying feedlots and those in areas of groundwater recharge.

2.4 Effects characterization

Two types of biotic effects, direct and indirect, will be discussed in this section. Direct toxic effects from ammonia are those that directly impact on an individual — typically, death, reduced growth rate or reduced reproductive success. Indirect effects are those that typically affect ecosystems by altering the nutritional regime, in the case of eutrophication, or by altering some other physical parameter, like pH in the case of acidification. Negative effects on ecosystems usually take the form of shifts in dominant organisms, usually to ones more capable of exploiting the nutritional regime or withstanding altered physical parameters. In these cases, toxicity to organisms comes about indirectly but is still ultimately traceable to deposition of ammonia in some form. Abiotic effects mediated through the atmosphere — i.e., destruction of stratospheric ozone, formation of ground-level ozone and enhancing the greenhouse effect — are also discussed.

2.4.1 Effects on terrestrial plants

The toxicity of atmospheric ammonia to plants is a very active research area, with the wide-scale importance of the problem being recognized only in the late 1980s and early 1990s. Ammonia was found to be a contributor to forest decline and soil acidification in Europe only after the effects of sulphur and nitrogen oxides were fairly well known. The effects of ammonia stood apart from those of the other atmospheric pollutants because they were seen in lowlands and near livestock production. It is now well documented that visible effects and dieback within metres to kilometres of large livestock operations can be the result of NH_3 emissions.

Ecological effects of NH_3 deposition are most likely to be associated with nitrogen-poor settings, where plants adapted to low nitrogen supply are dominant (Heil and Diemont, 1983; Schjoerring *et al.*, 1998). Alpine and boreal regions may be most susceptible (Boxman *et al.*, 1988; Aber *et al.*, 1989; Bobbink *et al.*, 1992). Soils with low pH buffer capacity and a tendency to be acidic may be susceptible because of the acidifying effects of nitrification of NH_4^+ to nitrate (Schuurkes *et al.*, 1986). Also, the addition of ionic NH_4^+ may disrupt cation balances.

Short-term (<1 day) acute toxicity values for plants are not readily available; however, Van der Eerden (1982) published a graph of mass concentrations versus exposure time for the effects of ammonia on terrestrial plants from published literature values. Some terrestrial plants (deciduous and coniferous trees and crops like buckwheat, cauliflower, tomato and sunflower) were adversely affected (leaf necrosis, increased sensitivity to cold) after an hour-long exposure to air concentrations ranging from 25 to 50 mg/m^3 (25 000 – 50 000 µg/m^3).

2.4.2 Acute effects on freshwater organisms

Concentrations of ammonia that are toxic to aquatic organisms are generally expressed as un-ionized ammonia (NH_3), because NH_3 and not NH_4^+ has been demonstrated to be the principal toxic form of ammonia in the environment, with few exceptions.

Although a sizeable body of knowledge exists on acute, chronic and sublethal effects of ammonia on fish, there is less literature available on its effects on invertebrate species and benthic organisms. Data on concentrations of NH_3 that are toxic to freshwater phytoplankton and vascular plants, although limited, indicate that freshwater plant species are appreciably more tolerant of NH_3 than invertebrates or fish.

2.4.2.1 Algae

Experimental data on the toxicity of ammonia to freshwater phytoplankton and vascular plant communities are limited and contradictory, although that may be the result of variation in response from different species. Most studies reported total ammonia concentrations and did not report pH and temperature, so that it was not possible to calculate un-ionized ammonia concentrations. At relatively high concentrations (compared with exposure levels for fish), some algae and most aquatic macrophytes can use ammonia as a nutrient. At concentrations between 2 and 5 mg total ammonia/L, growth inhibition occurred in *Chlorella vulgaris*, whereas complete growth inhibition occurred at 5.5 mg/L and 50% lethality occurred around 9 mg/L for a 120-hour exposure (Przytocka-Jusiak, 1976). Bretthauer (1978) reported that a concentration (assuming pH 6.5 and 30°C) of 0.6 mg NH_3/L killed *Ochromonas sociabilis* and that development of the population was reduced at 0.3 mg/L (duration of tests not reported). Concentrations of 0.06–0.15 mg NH_3/L had an insignificant effect on growth, and concentrations of 0.015–0.03 mg NH_3/L enhanced growth. Studies have shown that ammonia at concentrations exceeding 2.5 mg NH_3/L inhibited photosynthesis and growth in the algal species *Scenedesmus obliquus* and inhibited photosynthesis in the algae *Chlorella pyrenoidosa, Anacystis nidulans* and *Plectonema boryanum* (Abeliovich and Azov, 1976).

2.4.2.2 Fish

Symptoms of acute toxicity of ammonia in fish are loss of equilibrium, hyperexcitability, increased breathing, cardiac output and oxygen uptake, and, eventually, convulsions, coma and death.

Fish can tolerate high concentrations of un-ionized ammonia over a period of hours. As the exposure period extends, tolerance diminishes. Early studies with rainbow trout (*Oncorhynchus mykiss*) and coho salmon (*O. kisutch*) (Grindley, 1946; Downing and Merkins, 1955; Lloyd and Herbert, 1960; Ball, 1967; Department of Scientific and Industrial Research, 1967; Brown *et al.*, 1969; Buckley, 1978; Thurston *et al.*, 1981a,b) reported the hours to 50% mortality for various exposure conditions. The relationship developed using the data from these studies describes the trout time to 50% mortality (LT_{50}) for a given exposure concentration (x, in mg NH_3/L) as:

$$LT_{50} = 4.7942 * x^{-1.7681} \text{ hours}$$

Conversely, for a given exposure period (x, in hours), the LC_{50} (concentration of un-ionized ammonia producing 50% mortality) can be determined:

$$LC_{50} = 1.7928 * x^{-0.3573} \text{ mg } NH_3/L$$

These relationships are valid for exposure periods between 30 minutes and 24 hours, since they are developed from a narrow range of high concentrations in water and a limited number of studies.

A few of the above studies have also reported the slope of the response relationships such that the LC_{10} could be estimated (Craig, 1999). Studies by Ball (1967), Brown *et al.* (1969) and Buckley (1978) demonstrate that between 3 and 48 hours, the LC_{10} is about 10% of the LC_{50}, as calculated by the above equation. As the duration of exposure increases, the percentage increases to about 70%, as illustrated by Broderius and Smith (1979) and reported by Lloyd (1961).

The species mean LC_{50} values for fish found in Canadian waters were calculated from data taken from Table 1 of the U.S. EPA (1985) water quality criteria document. Most of the acute tests were conducted in laboratories where concentrations were maintained at a constant level, and after 48–96 hours mortality would not change. The species acute mean un-ionized ammonia concentrations are the geometric mean of LC_{50}s reported for respective species in the U.S. EPA (1985) document. The resulting values are presented in Table 4 along with the number of studies used to calculate the species mean LC_{50} and the minimum and maximum LC_{50} reported among the studies for that species. Species that are reported in Table 4 of U.S. EPA (1985) but are not indigenous to Canada have been excluded from Table 4.

Species mean LC_{50} values range from 0.28 mg NH_3/L for white perch (*Morone americana*) to 1.86 mg NH_3/L for green sunfish (*Lepomis cyanellus*). Certain sensitive species are localized, such as white perch, which are usually found in brackish waters on the Atlantic coast but have also been reported in Lake Ontario and the Bay of Quinte (Scott and Crossman, 1973). Mountain whitefish (*Prosopium williamsoni*) are also restricted to western Alberta and are widespread in British Columbia (Scott and Crossman, 1973). Salmonids are widespread and represent the next most sensitive group of species.

Table 4: Mean LC_{50}s for un-ionized ammonia in Canadian fish species

Common name	**Species name**	**LC_{50}[1] (mg NH_3/L)**	**No. of studies**	**Minimum LC_{50} (mg NH_3/L)**	**Maximum LC_{50} (mg NH_3/L)**
White perch	*Morone americana*	0.279	2	0.150	0.520
Mountain whitefish	*Prosopium williamsoni*	0.289	3	0.143	0.473
Chinook salmon	*Oncorhynchus tshawytscha*	0.442	3	0.399	0.476
Rainbow trout	*Oncorhynchus mykiss*	0.481	112	0.158	1.090
Pumpkinseed	*Lepomis gibbosus*	0.489	4	0.140	0.860
Coho salmon	*Oncorhynchus kisutch*	0.520	8	0.272	0.880
Cutthroat trout	*Oncorhynchus clarki*	0.642	4	0.520	0.800
Brown trout	*Salmo trutta*	0.657	3	0.597	0.701
Mountain sucker	*Catostomus platyrhynchus*	0.685	3	0.668	0.819
Walleye	*Stizostedion vitreum*	0.706	4	0.510	1.100
Golden shiner	*Notemigonus crysoleucas*	0.720	1		
Golden trout	*Oncorhynchus aguabonita*	0.755	1		
Brook trout	*Salvelinus fontinalis*	1.005	2	0.962	1.050
Smallmouth bass	*Micropterus dolomieu*	1.105	4	0.690	1.780
Largemouth bass	*Micropterus salmoides*	1.304	2	1.000	1.700
Fathead minnow	*Pimephales promelas*	1.344	45	0.240	3.440
White sucker	*Catostomus commersoni*	1.349	7	0.760	2.220
Mottled sculpin	*Cottus bairdi*	1.390	1		
Bluegill	*Lepomis macrochirus*	1.406	15	0.260	2.970
Spotfin shiner	*Cyprinella spiloptera*	1.479	3	1.200	1.620
Channel catfish	*Ictalurus punctatus*	1.707	14	0.500	4.200
Stoneroller	*Comostoma anonalum*	1.720	1		
Green sunfish	*Lepomis cyanellus*	1.860	6	0.590	2.110

[1] **LC_{50} is the geometric mean when more than one study result is reported.**

2.4.2.3 Invertebrates

A number of invertebrate acute lethality studies are also referenced in the U.S. EPA (1985) water criteria document and presented in Table 5; concentrations are similar to those found for fish.

The species mean LC_{50} values for invertebrates range from 1.2 mg NH_3/L for the cladoceran species and fingernail claim (*Musculium transversum*) to as high as 10.2 mg NH_3/L reported for a caddisfly larvae. The more sensitive invertebrates appear to be the pelagic cladocerans, while the epibenthic and benthic organisms appear more tolerant. The sensitivity of invertebrates to ammonia as a group overlaps with the median of most tolerant fish species.

Table 5: Mean LC_{50}s for un-ionized ammonia in invertebrate species

Common name	**Species name**	**LC_{50} (mg NH_3/L)**	**No. of studies**	**Minimum LC_{50} (mg NH_3/L)**	**Maximum LC_{50} (mg NH_3/L)**
Cladoceran	*Daphnia pulicaria*	1.160	1		
Cladoceran	*Simocephalus vetulus*	1.185	2	0.613	2.29
Fingernail clam	*Musculium transversum*	1.191	3	0.93	1.29
Flatworm	*Dendrocoelum lacteum*	1.400	1		
Daphnid	*Daphnia magna*	1.613	12	0.53	4.94
Mayfly	*Callibaetis* sp.	1.800	1		
Snail	*Physa gyrina*	1.961	5	1.59	2.49
Stonefly	*Arcynopteryx parallela*	2.030	2	2.00	2.06
Amphipod	*Crangonyx pseudogracilis*	2.316	5	1.63	5.63
Tubificid	*Tubifex tubifex*	2.700	1		
Snail	*Helisoma trivolvis*	2.760	1		
Crayfish	*Orconectes nais*	3.150	1		
Mayfly	*Callibaetis skokianus*	4.829	3	3.86	5.88
Isopod	*Asellus racovitzai*	4.950	1		
Beetle	*Stenelmis sexilneata*	8.000	1		
Caddisfly	*Philarctus quaeris*	10.200	1		

2.4.3 Sublethal effects on freshwater organisms

Sublethal effects occur at concentrations and over extended periods that do not result in acute lethality to the organism, but can affect the population of species and community characteristics. The most evident responses are integrative and are exhibited by reductions in growth (length or weight) or are related to reproductive success (egg production, hatching, larval survival). Other effects, such as behavioural responses, tissue damage (e.g., pathological changes in the tissue of the gills, liver and kidney of fish) or biochemical or physiological changes, can affect the individual but in most cases are reversible and will not necessarily change the character of the community. The concentrations at which these sublethal responses occur are presented in Table 6.

Table 6: Summary of mean sublethal endpoints in freshwater species

Common name	Species name	EC_{20}[1] (mg NH_3/L)	No. of studies	Min. EC_{20} (mg NH_3/ L)	Max. EC_{20} (mg NH_3/ L)	Reference
Scud	*Hyallela azteca*	0.051	1			Borgmann, 1994
Sockeye salmon	*Oncorhynchus nerka*	0.057	1			Rankin, 1979
Rainbow trout	*Oncorhynchus mykiss*	0.090	4	18	181	Burkhalter and Kaya, 1977; Broderius and Smith, 1979; Calamari *et al.*, 1981; Solbé and Shurben, 1989
Fathead minnow	*Pimephales promelas*	0.173	3	105	247	Swigert and Spacie, 1983; Mayes *et al.*, 1986; Thurston *et al.*, 1986
Walleye	*Stizostedion vitreum*	0.189	2	179	199	Hermanutz *et al.*, 1987
Bluegill and pumpkinseed	*Lepomis macrochirus* and *L. gibbosus*	0.239	3	60	553	Reinbold and Pescitelli, 1982; McCormick *et al.*, 1984; Smith *et al.*, 1984
Leopard frog	*Rana pipiens*	0.270	1			Diamond *et al.*, 1993
Catfish	*Ictalurus punctatus*	0.290	6	162	487	Colt and Tchobanoglous, 1978; Reinbold and Pescitelli, 1982; Swigert and Spacie, 1983; Hermanutz *et al.* , 1987; Bader and Grizzle, 1992
Smallmouth bass	*Micropterus dolomieu*	0.321	2	301	343	Broderius *et al.*, 1985
Green sunfish	*Lepomis cyanellus*	0.553	1			Reinbold and Pescitelli, 1982
Amphipod	*Crangonyx*	0.370	1			Diamond *et al.*, 1993
	Ceriodaphnia dubia	0.520	1			Nimmo *et al.*, 1989
	Daphnia magna	0.759	2	607	950	Reinbold and Pescitelli, 1982; Gersich *et al.*, 1985

[1] EC_{20} is the geometric mean when more than one study result is reported.

2.4.4 Acute and sublethal effects on saltwater organisms

Available acute and chronic ammonia toxicity data for saltwater organisms are more limited than those for freshwater organisms. The U.S. EPA (1989) published a review on the saltwater toxicity of ammonia, much of which is reported in Table 7.

2.4.4.1 Acute toxicity

Cheung and Wong (1993) found that relatively unpolluted and heavily polluted sediments dredged from around Hong Kong were both highly toxic to the marine clam, *Tapes philippinarium*. A correlation coefficient of 0.99 at $p < 0.001$ was determined between mortality and ammonia concentrations in the seawater in tests with the relatively unpolluted sediments, and from 0.92 to 0.96 at $p < 0.001$ for the heavily polluted sediments. The total ammonia concentration in seawater at the ET_{50} (time to 50% effect; 14–15 days) was 10–11 mg/L in both sediment systems.

In published literature, mean LC_{50} values for marine invertebrate species found in North American waters range from 0.77 to 19.1 mg NH_3/L; for marine fish species, they range from 0.49 to 2.9 mg NH_3/L (see Table 7). The winter flounder (*Pseudopleuronectes americanus*) had the most sensitive acute toxicity value of 0.49 mg/L. The remaining genera tested have mean acute values within an order of magnitude of that for the winter flounder. The three most tolerant North American species reported by the U.S. EPA (1989) are molluscs. Species mean acute values of 3.08, 5.36 and 19.1 mg/L were reported for the brackish water clam (*Rangia cuneata*), the quahog clam (*Mercenaria mercenaria*) and the eastern oyster (*Crassostrea virginica*), respectively. Except for these molluscs, there is no phyletic pattern in acute sensitivity to ammonia. Fishes and crustaceans are well represented among both the more sensitive and the more tolerant species tested.

Few consistent trends or patterns were evident in the acute toxicity values with respect to biological or environmental variables. Contributing to this, in part, is test variability. Variability in acute toxicity values may reflect differences in condition of the test organisms, changes in the exposure conditions, particularly pH, during testing, and variance incurred through calculation of un-ionized ammonia concentrations. Few differences are evident in acute toxicity at different salinities in tests with similar life stages and similar pH and temperature conditions. Temperature also has little influence on acute ammonia toxicity to most saltwater animals. There are few differences in acute toxicity with respect to differences in life stage or size of the test organism (U.S. EPA, 1989). Several data sets on the effect of pH on the toxicity of un-ionized ammonia suggest that, unlike the data on freshwater species, the pH–toxicity relationship is not consistent between species.

The U.S. EPA (1989) concluded that there was insufficient information to conclude that any of these factors, when acting alone, has a consistent major influence on the acute toxicity of NH_3 to saltwater organisms.

Table 7: Ranked mean acute toxicity values for un-ionized ammonia

Species	Mean LC_{50} or EC_{50} (mg NH_3/L)	Temperature (°C)	Salinity (‰)	PH
Winter flounder, *Pseudopleuronectes americanus*	0.49	7.5	31	8.0 (7.9–8.1)[1]
Red drum, *Scicenops ocellatus*	0.55	25 (25–26)[1]	29 (28–30)[1]	8.1 (8.0–8.2)[1]
Sargassum shrimp, *Latreutes fucorum*	0.77	23.4	28	8.07
Prawn, *Macrobachium rosenbergii*	0.78	28	12	7.6 (6.8–8.3)[1]
Planehead filefish, *Monocanthus hispidus*	0.83	23.4	28	8.07
Copepods:				
Eucalanus elongatus	0.87	20.3	34	8.0
Eucalanus pileatus	0.79	20.5	34	8.2
Morone spp.:				
Striped bass, *M. saxatilis*	0.48	19.3 (15–23)[1]	12.9 (5–34)[1]	(7.2–8.2)[1]
White perch, *M. americana*	2.13	16	14	8.0
Mysid, *Mysidopsis bahia*	1.02	23.2 (19.3–26.5)[1]	21.4 (10–31)[1]	(6.8–9.2)[1]
Spot, *Leiostomus xanthurus*	1.04	20.4	9.3	79.2
Silversides:				
Inland, *Menidia beryllina*	1.32	25.3 (18–32.5)[1]	26.1 (11–31.5)[1]	(6.9–9.1)[1]
Atlantic, *Menidia menidia*	1.05	20.3 (10.8–24.8)[1]	11.6 (8.5–29.8)[1]	8.0 (7.0–9.0)[1]
Striped mullet, *Mugil cephalus*	1.54	21.8 (21.0–23.3)[1]	10	8.1 (8.0–8.1)[1]
Grass shrimp, *Palaemonetes pugio*	1.65	19.9 (19.3–20.4)[1]	19.2 (10–28.4)[1]	8.0 (7.9–8.1)[1]
Sea bream, *Sparus auratae*	1.88	22.5 (17.9–27)	37.5 (34.5–40.5)	8.1
At dissolved oxygen levels:				
93% saturation	1.93	27	40.5	8.1
61% saturation	1.28			
33% saturation	0.97			
26% saturation	0.41			
Lobster, *Homarus americanus*	2.21	21.9	33.4	8.1
Sheepshead minnow, *Cyprinodon variegatus*	2.74	21.0 (10.3–32.5)[1]	19.4 (9.8–32.5)[1]	(7.6–8.1)[1]
Three-spined stickleback, *Gasterosteus aculeatus*	2.93	19 (15–23)[1]	26.3 (11–34)[1]	(7.6–8.2)[1]
Turbot, *Scophthalmus maximus*	2.96	17.9 (17–18.8)	34.3 (34.0–34.5)	8.15
Brackish water clam, *Rangia cuneata*	3.08	20.2	9.2	7.95
Mudskippers:				
Periophthalmodon schlosseri	9.13	25	15	N/A
Boleophthalmus boddaertid	1.02	25	15	N/A
Quahog clam, *Mercenaria mercenaria*	5.36	20	27	(7.7–8.2)[1]
Lake Magadi tilapia, *Oreochromis alcalicus grahamic*	11.47[2]	34	N/A	9.9
Eastern oyster, *Crassostrea virginica*	19.10	20	27	(7.7–8.0)[1]

[1] Mean (range) values for temperature, salinity or pH calculated when values from original text were given individually. When only ranges were given in original text, mean was not calculated.

[2] Average of LC_{50} values at 24 and 48 hours.

2.4.4.2 Sublethal toxicity

The U.S. EPA (1989) also reported on unpublished chronic toxicity tests, but with only two saltwater species, neither of which is native to Canada. A life cycle toxicity test has been conducted with the mysid, *Mysidopsis bahia*, and an early life stage test has been completed with the inland silverside (*Menidia beryllina*).

The *M. bahia* test lasted 32 days and was reported in Cardin (1986). Survival was reduced to 35% of controls, and length of test organisms was significantly reduced at 0.33 mg NH_3/L.

The effect of ammonia on survival and growth of the inland silverside, *M. beryllina*, was assessed in an early life stage test lasting 28 days (Poucher, 1986). Fry survival was reduced to 40% at 0.38 mg/L. Average weights of surviving fish at concentrations above 0.074 mg/L were significantly less than that of controls.

2.4.5 Ecosystem effects

This section focuses on effects of ammonia on whole ecosystems, where the impact is not direct toxicity of ammonia. The two major processes found are acidification of soft waters and eutrophication of aquatic and terrestrial ecosystems.

A well-documented effect of human impact upon aquatic ecosystems is eutrophication, a multifaceted term generally associated with increased productivity, structural simplification of biotic components, and a reduction in the ability of the metabolism of the organisms to adapt to imposed changes (reduced stability). In this condition of eutrophication, excessive inputs commonly seem to exceed the capacity of the ecosystem to be balanced. In reality, however, the systems are out of equilibrium only with respect to the freshwater chemical and biotic characteristics desired by humans for specific purposes (Wetzel, 1983).

Acidification of water by ammonium sulphate deposition is a strong reaction, stronger than the addition of sulphuric acid. This is due to the nitrification of the ammonium molecule, releasing hydrogen ions, in addition to the release of the acidic sulphate molecule.

2.4.5.1 Freshwater eutrophication

The material presented on aquatic and marine coastal eutrophication is from a review of the literature on the causes and conditions of aquatic eutrophication in Canada, prepared for Environment Canada (Chambers *et al.*, 2000).

Nutrients are essential to lakes because they provide the raw material for the growth of algae, which are the food sources of zooplankton, which, in turn, are eaten by fish. The concentration of nutrients in a lake is determined by the interplay of the magnitude, timing and bioavailability of the nutrient load, the rate of water supply compared with the volume of the lake (flushing time) and the depth of the lake.

In lakes and rivers not affected by nutrient inputs, the nutrient cycling processes are typically in balance. However, with the excessive input of nutrients, like ammonia and dissolved phosphorus, these processes become unbalanced, usually resulting in large standing crops of algae and plants. The phytoplankton have a high total respiration demand, reducing oxygen concentrations and generating toxins (depending on the algal species present) that can suppress herbivorous plankton. The inevitable die-off of algae in late summer increases the bacterial populations tremendously, which can also increase toxins in the water and will severely decrease the dissolved oxygen content to the point where fish can be killed. Over the long term, elevated eutrophic rates can alter the biological community towards organisms more tolerant of shaded, oxygen-deficient waters.

In most Canadian lakes, phosphorus is the nutrient that is most in demand, and algal growth in the majority of lakes is therefore said to be phosphorus limited. Discovering this relationship led to the significant reduction in releases of phosphorus from municipal water treatment plants, largely through the regulation of phosphorus in detergents and the chemical precipitation of phosphorus in the plants prior to discharge. Major improvements in water quality resulted from these actions.

The role of ammonia in aquatic eutrophication is as a source of nitrogen for the generation of nitrates that are directly usable by algae and aquatic plants. In lakes that receive continuous inputs of ammonia and phosphorus (secondary sewage treatment facilities typically release both), the nitrification process can be operating at a maximum in summer, so that the lakes are enriched in nitrates and phosphorus, leading to lush growths of algae and rooted plants. In the fall, the die-off of algae and plants depletes oxygen and creates a harsh environment for fish. In water systems that receive ammonia but not phosphorus, the nitrification process will still be at a maximum, but, due to the deficiency in phosphorus, they have limited algal and macrophytic growth. In these cases, eutrophication does not proceed, but the concentrations of ammonia and nitrates can rise to toxic levels and can still lead to severely depleted oxygen conditions from the nitrification process. Still other lakes are truly limited by nitrogen; one such system in Canada is the Qu'Appelle Lakes in southern Saskatchewan (see Section 3.1.2.2.3).

2.4.5.2 Coastal marine eutrophication

In the last 20 years, the causes and extent of coastal eutrophication have been increasingly recognized as a global problem (Howarth, 1988; Vollenweider, 1992; NRC, 1993; UNEP, 1995; Paerl, 1997). Coastal areas, including fjords, estuaries, lagoons, continental shelves and inland seas, comprise 1–2% of the total area of the ocean, yet are responsible for 20% of global primary production (Duarte, 1995). These regions receive the bulk of their nutrient inputs from freshwater sources (i.e., terrestrial runoff, rivers and groundwater). The natural background levels of nutrient concentrations of these inputs are normally much higher than those of even the most eutrophic seawater (Dederen, 1992).

Nitrogen is generally the nutrient limiting primary production in the open ocean, in contrast with fresh waters, where phosphorus is typically the limiting nutrient (Howarth, 1988; Vollenweider, 1992). It is in the coastal zone where nutrient-rich freshwater inputs are diluted into the nutrient-poor saline environment of the open ocean. In these highly dynamic transitional waters, either phosphorus or nitrogen limitation can occur, depending on a set of complex interactions.

In recent decades, nitrogen and phosphorus transport to coastal waters has increased (Howarth *et al.*, 1996) and is correlated with various indices of human activity in the watershed (Cole *et al.*, 1993; Howell *et al.*, 1996; Vitousek *et al.*, 1997; Caraco, 1995). If nitrogen is measured, then most of the inputs to coastal waters are derived from non-point sources, typically as nitrate (NRC, 1993).

Evidence from the northern hemisphere indicates that over-enrichment of coastal waters has created a niche occupied by a diverse group of dinoflagellates and diatoms that, like their counterparts in eutrophic lakes (the blue-green algae), produce toxic chemicals (Burkholder *et al.*, 1992). Marine algae have been found responsible for at least four different illnesses in human consumers of molluscs as well as massive mortality of fish, birds and marine mammals (Paerl, 1997). The occurrence of these "harmful algal blooms" has resulted in the closure of shellfisheries, resulting in large economic impacts on coastal communities. The exact cause of these blooms is not clear, although they tend to follow periods of intense rainfall, runoff and intense irradiation from sunlight (Smayda, 1997).

Eutrophication of Canada's east and west coasts is not occurring at present. There are some indications that coastal areas around Vancouver and Halifax are impacted as a result of sewage effluents, but these are not eutrophication issues. This situation will likely remain as long as anthropogenic nutrient loading does not increase substantially (Chambers *et al.*, 2000).

2.4.5.3 Terrestrial eutrophication

Among the mineral elements, nitrogen is required in the largest amount by plants; very often growth is limited by its supply. When more nitrogen is added, plants grow more rapidly, and the nitrogen in the increased plant biomass is effectively retained by the ecosystem. In addition, plants can accumulate nitrogen, as nitrate, in tissues in excess of the specific nutritional requirements. Ecologically, this may be an adaptation to deal with a chronically low nitrogen supply. In effect, plant growth responds to increased nitrogen supply until nitrogen is no longer the limiting factor for growth. Nitrogen-deficient ecosystems can tolerate, even benefit from, periodic excessive doses of nitrogen; however, metabolic imbalances can occur if the excessive nitrogen levels occur for too long.

Nitrogen addition has the potential to affect many attributes of the terrestrial environment, not all of which are well understood. Among the indirect effects, increased leaching of nitrate from soils is one of the more obvious. The concept of "nitrogen saturation" has been used to describe the level of nitrogen in an ecosystem that maximizes the retention within the ecosystem (Aber *et al.*, 1989). Additions above this limit result in nitrate leaving the ecosystem in amounts that could be detrimental downstream. This concept is based on the observation that ecosystems cycle nitrogen very efficiently.

Critical loads of ammonia were established in Europe to avoid two general types of effects. One was the leaching of nitrogen, typically as nitrate, from ecosystems that normally are very conservative in nitrogen cycling. The other general effect to be avoided is the shift in dominance among species, especially in nitrogen-poor environments (Schulze *et al.*, 1989; Bobbink *et al.*, 1992; De Vries, 1992). Some other indirect effects are subtle, such as the loss of mycorrhizal fungi associated with conifer tree roots (Pérez-Soba *et al.*, 1995). The critical loads for nitrogen promulgated by the Dutch Priority Programme on Acidification ranged from 9.8 to 42 kg/ha per year, with the lowest values of this range associated with avoiding changes in species composition in coniferous forests (Lekkerkerk *et al.*, 1995).

2.4.5.4 Acidification

Deposition of ammonium sulphate, the most common form of ammonia particulate, will generate considerable quantities of acid, as eight hydrogen ions may be released during nitrification. The Dutch, Belgians, Norwegians and Germans have found that excessive quantities of ammonium sulphate are having adverse impacts on poorly buffered soils and waters in close proximity to large sources (Schuurkes, 1986; Schuurkes *et al.*, 1986; Gjessing, 1994).

In long-term, indoor, soft-water ecosystem studies, Brouwer *et al.* (1997) showed that acidification of an ecosystem was greater when ammonium sulphate was deposited in rainfall than when sulphuric acid was deposited. This is due to the nitrification of the ammonium, releasing extra hydrogen ions into the ecosystem. Increased levels of dissolved metals were detected, as well as shifts in the plant community. Plants typical of soft waters declined and were overgrown by *Sphagnum* species and *Juncus bulbosus.* The recovery of the impacted ecosystems was also different; the sulphuric acid system recovered quickly, but the ammonium sulphate ecosystems did not fully recover after 10 years of clean water. The ecosystems most sensitive to such acidic inputs are found on the Canadian Shield throughout much of eastern Canada. There has been little in the way of ammonium particulate monitoring within the Canadian acid monitoring program, so the contributions of ammonia to acidification in Canada are not known.

2.4.6 Abiotic effects mediated through the atmosphere

Ammonia is the most prevalent alkaline gas in the atmosphere, as well as the third most common form of nitrogen in the troposphere. Because of its high reactivity, ammonia readily combines with acidic chemical species, such as hydrochloric acid, nitric acid or sulphuric acid, forming ammonia aerosols. Klemm and Gray (1982) determined that the acidity of rainfall in Alberta was determined as much by the presence of alkaline species (calcium and ammonium ions) as by the absence of acidic species (sulphur and nitrogen oxides). Even so, un-ionized ammonia as an atmospheric gas itself is rather passive: it either deposits quickly near sources or is converted to particulate form. As a result, particulates can be transported long distances, affecting tropospheric aerosol loading and thus issues of visibility, smog and climate.

An important connection for air quality issues, therefore, is the conversion of ammonia gas into the aerosol form, increasing tropospheric loading of respirable particulate matter, PM_{10} and $PM_{2.5}$. Ammonia in the atmosphere can determine the type and quantity of fine particulate matter. The chemically preferred form for sulphate is ammonium sulphate, solid or aqueous.

However, competition between sulphate and nitrate for the available ammonia produces complicated aerosol behaviour. In areas with low concentrations of atmospheric ammonia, most particulate matter will be acidic, as there is insufficient ammonia to neutralize the available sulphate. In areas with high ammonia concentrations, however, any ammonia that does not react with sulphate will be able to react with available nitrate, forming ammonium nitrate aerosols. PM_{10} and $PM_{2.5}$ have been determined to be CEPA "toxic" to humans, so effects of ammonia-containing particulate matter are not considered in this report. Table 8 lists other air issues that are connected to atmospheric ammonia.

Table 8: Ammonia connections to other air issues

Air issue	Major atmospheric gases	Ammonia role	Sensitivity
Stratospheric ozone depletion	Chlorofluorocarbons, hydrochlorofluorocarbons	Too reactive a species for stratospheric chemistry	Minimal
Climate change	Carbon dioxide, nitrous oxide, methane, water	May influence global aerosol concentrations	Minimal
Ground-level ozone (smog)	Oxides of nitrogen, volatile organic compounds	Participates in nitrogen chemistry	Minimal
Acid deposition	Sulphates, nitrates, ammonia	Soil/water acidifier through nitrogen cycle; participates in sulphur dioxide oxidation by ozone	Moderate
Hazardous air pollutants (toxics)	Organic compounds and heavy metals	May enhance particulate matter pathway for dispersion of hazardous air pollutants	Moderate
Particulate matter ($PM_{2.5}$ and PM_{10})	Sulphates, nitrates, ammonia, volatile organic compounds	Reacts with acid gases to form hygroscopic salts	High

2.5 Toxicokinetics, mode of action and metabolism

2.5.1 Freshwater fish

This information is derived from an unpublished review (Randall, unpublished), used with the author's permission.

Most biological membranes are permeable to NH_3, but not NH_4^+. Ammonia is excreted by diffusion across the body surface of most aquatic animals, usually the gills, although there may be some carrier-mediated excretion of NH_4^+ in some species. The rate of NH_3 excretion is determined by the magnitude of the NH_3 gradient between blood and water (Wilson *et al.*, 1994). Ammonia excretion is augmented by acidic conditions in the water, because any NH_3 excreted into the water is rapidly converted to and trapped as NH_4^+, maintaining the NH_3 gradient across the gills and augmenting ammonia excretion. Many freshwater fish actively excrete protons, forming an acid boundary layer next to the gill surface (Lin and Randall, 1991), and this augments ammonia excretion (Wright *et al.*, 1989). Above water pH 9.0, ammonia excretion is reduced because of the absence of ammonium ion trapping (Wright *et al.*, 1989), resulting in elevated plasma ammonia levels (Yesaki and Iwama, 1992). Thus, many animals have difficulty excreting ammonia when exposed to alkaline conditions.

2.5.2 Marine fish

Ammonium ion diffusion across the gills may be significant in seawater teleost fish, where ionic permeability is high (Evans, 1984).

The body surface of marine animals is generally more permeable to ions than that of freshwater animals (Evans, 1984). Thus, the passive flux of ammonium ions is likely to be greater in marine animals. There is also evidence for the active excretion of ammonium ions in the mudskipper, *Periophthalmodon schlosseri* (Randall *et al*., 2000). There is no clear evidence that water pH is modulating toxicity in marine species. It is possible that, because of the increased ammonium ion permeability, the relationship between water pH and ammonia toxicity is minimal. That is, there is no *a priori* reason to assume that pH will modulate ammonia toxicity in the marine environment. There is a paucity of data on the effects of water pH on ammonia toxicity in the marine environment.

2.5.3 Accumulation in aquatic organisms

Accumulation of ammonia in the body can be due to either the inability to excrete or convert nitrogenous wastes or a net influx of NH_3 from the environment. Externally, the concentration of NH_3, rather than NH_4^+, is of concern, as biological membranes are permeable to NH_3 but much less so to NH_4^+. Consequently, NH_3, but not NH_4^+, diffuses readily across the external surface into the body. As a result, if NH_3 levels are high in the environment, ammonia levels in exposed animals increase as well. In acid water, nearly all ammonia is as NH_4^+, and the rate of ammonia entry into the fish is low. As pH increases to more alkaline conditions and water pH approaches the pK (9.2–9.5) of the ammonia/ammonium ion reaction, toxicity increases significantly for many species due to the shift in equilibrium to the more diffusable NH_3 form. Water of pH above 9.5 can be toxic, even though it contains little or no ammonia, because ammonia levels rise to toxic levels in the fish as a result of impaired excretion.

2.5.4 Factors affecting the aquatic toxicity of ammonia

Several factors have been shown to modify the acute toxicity of ammonia to freshwater organisms. Some factors alter the concentration of NH_3 in the water by affecting the aqueous ammonia equilibrium, while other factors affect the toxicity of NH_3 itself, either ameliorating or exacerbating its effects. Factors that have been shown to affect ammonia toxicity include temperature, pH, dissolved oxygen concentration, ionic concentration, previous acclimatization to ammonia, fluctuating or intermittent exposure, carbon dioxide concentration, salinity and the presence of other toxic substances. The best studied of these is pH; the acute toxicity of NH_3 has been shown to decrease as pH decreases (becomes more acidic). Data on temperature effects on acute toxicity are limited and variable; the U.S. EPA (1998) recently released revised water quality guidelines for ammonia for which they reviewed the data on temperature. The effects of dissolved oxygen are probably more important than the effects of temperature, with increased toxicity at lower dissolved oxygen concentrations (Thurston *et al.*, 1981a). All of these factors may come into play in any water body. The pH of most rivers fluctuates with season, as does temperature. Dissolved oxygen will inversely follow the temperature variations, with less oxygen dissolved at high temperatures, exacerbating the toxicity effect from temperature. In Canadian waters, pH values usually rise in summer as the temperature increases and the dissolved oxygen content decreases. Downstream of municipal outfalls, there is often an oxygen sag as nitrification of ammonia and other biological processes use up the available oxygen, making the in-plume region more hazardous for organisms.

2.5.4.1 pH

The toxicity of aqueous solutions of ammonia and ammonium compounds to fish has been attributed to NH_3 present in the solution. The pH correlation with toxicity of ammonia was assumed to be based on the aqueous ammonia equilibrium. Thurston *et al.* (1981b) tested the toxicity of ammonia to rainbow trout (*O. mykiss*) and fathead minnows (*Pimephales promelas*) in 96-hour flow-through bioassays at different pH levels within the range 6.5–9. Results showed that the toxicity of ammonia, in terms of NH_3, increased at lower pH values and could also increase at higher pH values. It was concluded either that NH_4^+ exerts some measure of toxicity or that increased hydrogen ion concentration increases the toxicity of NH_3. Acute (96-hour) exposures of green sunfish (*L. cyanellus*) and smallmouth bass (*Micropterus dolomieu*) at four pH levels over the range 6.5–8.7 showed that, for both species, NH_3 toxicity increased markedly with a decrease in pH, with LC_{50} values at the lowest pH tested (6.5–6.6) being 2.6–3.6 times smaller than those at the highest pH tested (8.7) (McCormick *et al.*, 1984; Broderius *et al.*, 1985). The U.S. EPA (1998) reviewed the extant toxicity data and came to the conclusion that "all of the datasets show a strong trend of total ammonia LC_{50}s decreasing with increasing pH." This confirms the concept that ammonia is more toxic at basic pHs.

2.5.4.2 Temperature

Information on the correlation between temperature and toxicity of ammonia is varied, but the two appear to have an inverse relationship. The toxicity of ammonia is greater at colder temperatures, the reverse of what would be expected based solely on the aqueous ammonia equilibrium. After the U.S. EPA (1998) reviewed the data for their recent water quality criterion document on ammonia, they concluded that temperature had a minor effect on toxicity and decided that they would not use it in their calculation of a water quality criterion. Thurston and Russo (1983) reported an inverse relationship between temperature and toxicity for rainbow trout (*O. mykiss*) over the temperature range 12–19°C. Thurston *et al.* (1983) reported a similar decrease in toxicity with increasing temperature in fathead minnow (*P. promelas*) over the temperature range 12–22°C. A similar relationship was found by Reinbold and Pescitelli (1982) in rainbow trout, bluegill (*Lepomis macrochirus*) and fathead minnow, while Colt and Tchobanoglous (1978) found a similar relationship in channel catfish (*Ictalurus punctatus*).

At a temperature of 19°C and a pH of 8.5, it takes less than 0.4 mg total ammonia/L to generate a potentially toxic condition, while at 19°C and pH 7, it takes over 11 mg/L. At a temperature of 4°C and pH 8.5, it takes just over 1 mg total ammonia/L to generate this condition, while at 4°C and pH 7, it takes over 35 mg/L.

2.5.4.3 Dissolved oxygen concentration

The dissolved oxygen concentration of water has long been known to affect the toxicity of ammonia to fish (Merkens and Downing, 1957; Vamos and Tasnadi, 1967; Alabaster *et al.*, 1979). Thurston *et al.* (1981a) conducted a detailed study of this phenomenon and showed the potential impacts of reduced dissolved oxygen levels on the acute toxicity of ammonia. The 96-hour LC_{50} of un-ionized ammonia to rainbow trout (*O. mykiss*) was tested in various concentrations of dissolved oxygen, from 2.6 to 8.6 mg/L. The former concentration was the lowest at which 90% or more of the control fish survived. There was a positive linear correlation between LC_{50} and dissolved oxygen over the entire dissolved oxygen range tested: ammonia toxicity increased as dissolved oxygen decreased. Un-ionized ammonia LC_{50} values were also computed for 12, 24, 48 and 72 hours: the correlation with dissolved oxygen (DO) was greater the shorter the time period. The 96-hour LC_{50} values varied from 0.7 mg/L at 8.6 mg DO/L to 0.3 mg/L at 2.6 mg DO/L. The estimated correlation coefficient was 0.93, with an estimated regression line of $LC_{50} = 0.1903 - 0.06712(DO)$ (Thurston *et al.*, 1981a).

The analysis of dissolved oxygen versus LC_{50} over the entire 96-hour test period showed a clear trend: the shorter the time period, the more pronounced the positive relationship between acute toxicity and dissolved oxgyen. This suggests either that individual fish that were sensitive to ammonia succumbed early or that those fish that do survive become increasingly acclimated to ammonia and oxygen conditions. These tests show that any reduction in dissolved oxygen reduces the tolerance of rainbow trout fingerlings to acutely toxic concentrations of ammonia: the estimated tolerance at 5.0 mg DO/L is 30% less than at 8.5 mg DO/L.

3.0 PROPOSED ASSESSMENT OF "TOXIC" UNDER CEPA 1999

3.1 CEPA 1999 64(a): Environment

The environmental risk assessment of a PSL substance is based on the procedures outlined in Environment Canada (1997a). Environmental assessment endpoints (e.g., adverse reproductive effects on sensitive fish species in a community) are selected based on analysis of exposure information and subsequent identification of sensitive receptors. For each endpoint, a conservative Estimated Exposure Value (EEV) is selected and an Estimated No-Effects Value (ENEV) is determined by dividing a Critical Toxicity Value (CTV) by an application factor. A conservative (or hyperconservative) quotient (EEV/ENEV) is calculated for each of the assessment endpoints in order to determine whether there is potential ecological risk in Canada. If these quotients are less than one, it can be concluded that the substance poses no significant risk to the environment, and the risk assessment is completed. If, however, the quotient is greater than one for a particular assessment endpoint, then the risk assessment for that endpoint proceeds to an analysis where more realistic assumptions are used and the probability and magnitude of effects are considered. This latter approach involves a more thorough consideration of sources of variability and uncertainty in the risk analysis.

3.1.1 Assessment endpoints

The bulk of the ammonia emitted in Canada is released to air, with the remainder being released to water. However, because of the rapid and large dilution of ammonia and the high deposition rate, the impacts through the air are not considered to be the main ones. Impacts on water ecosystems are more important from point sources due to the concentrations of ammonia in municipal WWTP effluents and the nature of the toxicity of ammonia to aquatic organisms.

Assessment endpoints include the reduction of growth and reproductive success in a mixed community of aquatic organisms for chronic exposures. The community included eight species of fish, one amphibian and four species of invertebrates. These are the species listed in Table 6, excluding pumpkinseed. The species were selected on the basis of being widespread in large areas of Canada and having at least one good toxicity study done on them. The most sensitive organisms in this community were the scud, *Hyallela azteca*, sockeye salmon (*Oncorhynchus nerka*) and the rainbow trout (*O. mykiss*). Scud are important in an aquatic ecosystem, as they are bottom browsers and act as an important source of fish food. Sockeye salmon and rainbow trout are top-order carnivores highly prized by humans for sport and food. Other assessment endpoints included 10% lethality of the most sensitive aquatic organisms in a community, again rainbow trout, in multiday exposures and 10% lethality of rainbow trout over 12 hours.

Terrestrial plants are the major organisms exposed via atmospheric transport of ammonia. Assessment endpoints for plants are the destruction of leaf material, specifically necrosis, browning and early leaf drop. A review of terrestrial plant toxicity data determined that acute toxicity is generally not a problem with respect to terrestrial plants, as levels of ammonia required to generate an acute toxic response were far higher than the levels documented from

Europe to cause adverse effects on terrestrial ecosystems. Most plants require inputs of nitrogen for continued growth and will respond with increased growth rates under very high nitrogen deposition rates. Under conditions of chronic exposure to gaseous and particulate ammonia, reduced drought tolerance was noted as an assessment endpoint that is quite sensitive.

Several sensitive Canadian ecosystems have been identified, in particular sphagnum bogs and conifer forests. Sphagnum bogs are adapted to low nitrogen conditions and do not respond quickly to inputs of nitrogen as ammonia. They can be endangered from other nitrogen-adapted plants, in particular grasses. Conifer forests can be susceptible to reduced frost hardiness and eutrophication when exposed to high levels of ammonia over long periods of time.

A concept also used in the terrestrial toxicity assessment was developed in Europe in response to heavy inputs of nutrients to many ecosystems. This is the concept of the "critical load," a loading of a chemical on an ecosystem that will not cause a deleterious impact (Boxman *et al.*, 1988; Bobbink *et al.*, 1992). Inputs are calculated as yearly loads of the chemical in question. The measurement endpoint is a specific ecosystem, i.e., conifer forests or sphagnum bogs. The assessment endpoints are effects (a shift towards nitrogen-adapted species like grasses) on similar terrestrial ecosystems in Canada.

3.1.2 Environmental risk characterization

3.1.2.1 Hyperconservative assessments

Hyperconservative assessments are presented in Table 9 for four exposure pathways: exposure of freshwater and saltwater fish, exposure of marine benthic organisms from dredging and dumping sediments, and exposure of conifer trees through atmospheric deposition of ammonia.

The EEVs are as follows: for fresh and salt water, a maximum value of 0.68 mg un-ionized NH_3/L was detected at one location (sewage from Annacis Island, Vancouver) (Servizi, *et al.*, 1978), and for air, 0.56 mg NH_3/m^3 was detected downwind of a dairy farm in California (Luebs *et al.*, 1973). Application factors of 10 were used for fish due to the large and fairly complete databases; an application factor of 100 was used with dredging operations due to the moderate database on effects and exposure information; and an application factor of 1000 was used for conifer trees because of the relatively poor database on effects.

For the hyperconservative assessment of saltwater dredging operations, an ENEV of 0.008 mg/L was used for *Ampelisca abdita* (Kohn *et al.*, 1994). The EEV value of 0.177 mg/L is from Sims and Moore (1995) based on average reported pore water concentrations from U.S. Army Corps of Engineers dredging operations in salt water.

Table 9: Summary of hyperconservative assessments

Species	EEV	CTV (EC_{50}/LC_{50})	Application factor	ENEV (mg NH_3/L)	Quotient	CTV reference
Open-water exposure of freshwater fish (rainbow trout, *Oncorhynchus mykiss*)	0.68 mg/L	0.158 mg/L	10	0.016	43	U.S. EPA, 1985
Open-water exposure of saltwater fish (winter flounder, *Pseudopleuronectes americanus*)	0.68 mg/L	0.49 mg/L	10	0.049	14	U.S. EPA, 1989
Saltwater dredging, *Ampelisca abdita*	0.177 mg/L	0.8 mg/L	100	0.008	22.1	Kohn *et al.*, 1994
Air exposure, conifer trees	0.56 mg/m^3	0.06 mg/m^3	1000	0.000 06	9333	Van der Eerden *et al.*, 1998

3.1.2.2 Conservative assessments

A conservative environmental assessment involves a further analysis of exposure and/or effects to calculate a quotient that is still conservative, but is more "realistic" than the hyperconservative quotient (Environment Canada, 1997a). The EEV is based on typical concentrations or deposition values in the vicinity of sources. The selection of CTVs is more rigorous, taking into account toxicity in organisms that would typically be exposed and matching the length of test exposure to that found in the field. The application factors used may be smaller if an adequate acute toxicity base data set is available (factor of 100) or if threshold sublethal toxicity values are available (factor of 10). However, the ENEV obtained should not be within the range of typical natural concentrations or deposition rates. If the quotient is still greater than one, then a probabilistic risk assessment is warranted, if there are sufficient data. The assumptions inherent in the data and application factor used are examined and minimized where possible, thereby refining the assessment process to generate a more accurate or "real-world" assessment than would be done in a hyperconservative assessment.

3.1.2.2.1 Releases to air

Based on an analysis of the literature (Sheppard, 1999), a critical load of 10 kg N/ha per year may be generally protective for nitrogen-poor sites, such as stands of native vegetation on soils of granitic origin. However, this value is not far above nitrogen deposition rates for remote areas. For example, Shaw *et al.* (1989) reported deposition of 4.2 kg N/ha per year in a boreal area in central Alberta. Janzen *et al.* (1997) reported a similar value. In contrast, Barthelmie and Pryor (1999) estimated that agricultural areas in the Lower Fraser Valley annually received from 44 to 105 kg N/ha.

The acute CTV for plants (leaf necrosis, increased sensitivity to cold) after an hour-long exposure to ammonia in air is 25 000 μg/m^3 (Van der Eerden, 1982).

Information on responses of plants to gaseous ammonia is sparse. There is a slight possibility of localized impacts on sensitive agricultural crops (in particular vegetables) close to point and area sources of ammonia, and the contribution of airborne ammonia to local water bodies is unknown. Ground-level concentrations of ammonia near agricultural and industrial sources are generally low or sporadic in occurrence and intensity. Because of the absence of Canadian data near point sources, a monitoring and modelling study was conducted by Environment Canada to develop exposure data (McDonald, 1999) using the ISCST3 (Industrial Source Complex Short Term) model at the Agrium Inc. fertilizer facility in Fort Saskatchewan, Alberta. The Agrium Inc. fertilizer plant is one of the major point sources of atmospheric ammonia in Canada. Another modelling run was made to estimate the release and potential impacts of ammonia from a manure fertilizer application to a 1-ha field in summer.

An area around the Fort Saskatchewan site, roughly 7.5 km^2, is exposed to a maximum hourly winter concentration of 100 μg/m^3. The acute CTV is 25 000 μg/m^3 for "general terrestrial" plants. An application factor of 100 is used due to the limited database on effects, but it is increased from 1000 in the hyperconservative assessment due to the improved exposure estimates.

$$\text{Quotient} = \frac{100}{250}$$

$$= 0.4$$

This quotient (<1) indicates that even for a large point source of ammonia, there is little likelihood of "instantaneous" injury to nearby terrestrial plants with high hourly concentrations of ammonia.

In order to facilitate a direct comparison between the potential influence of a point and an area source on nearby vegetation, the identical conditions were run again replacing the industrial complex with a 1-ha field treated with manure. Typical emission data for a surface application in Ontario were taken from information presented in Section 2.3.2.1. Prior to application, ammonia flux was measured to be less than 0.015 kg NH_3-N/ha per hour (Period A); immediately after application, fluxes of up to 1.2 kg NH_3-N/ha per hour were measured (Period B). These flux values dropped off quickly to around 0.1–0.3 kg NH_3-N/ha per hour (Period C) and stayed that way over a period of days, with considerable diurnal fluctuation (Beauchamp *et al.*, 1982). A 2-week period in June 1990 was selected with stable weather that was warm and dry.

The ISCST3 model allows us to determine the concentration of ammonia released during manure fertilization of a field. The 1-hour maximum concentration of ammonia released over a significant area (800 m^2 from a fertilized plot of 100 m^2) is 100 μg/m^3. This concentration could be expected outside the perimeter of a fertilized field as well. The acute CTV of 25 000 μg/m^3 is used. An application factor of 100 is used due to the limited database on effects, but it is increased from 1000 in the hyperconservative assessment due to the improved exposure estimates.

$$\text{Quotient} = \frac{100}{250}$$

$$= 0.4$$

This quotient indicates that for an area source of ammonia (a recently fertilized field using manure), there is little likelihood of an injury to nearby terrestrial plants with high hourly concentrations of ammonia.

In order to improve understanding of the atmospheric fate of nitrogen in the Lower Fraser Valley, two initiatives were undertaken. The first involved updating and improving the ammonia emissions inventory for the region, based on the most recent census data available and improved emission factors. The second initiative was directed towards providing spatial maps of concentration and deposition of nitrogen compounds based on model runs.

The maximum point of deposition during the model exercise was 105 kg/ha per year as NH_3 to the surface in the modelled area. A worst-case scenario was used with this deposition rate applied for a full year. Because this deposition is so driven by sources, this amount could vary substantially with season and may be subject to periodically high levels. This could have important terrestrial impacts, as the Dutch have found terrestrial eutrophication impacts on coniferous forests at such deposition rates.

Because the modelling exercise estimated ammonia inputs to the Lower Fraser Valley as a deposition rate, the critical loading rate will be used to estimate potential toxicity. The critical loading rate for sensitive terrestrial ecosystems in Canada is 10 kg N/ha per year based on long-term effects on conifer ecosystems. The modelling in the Lower Fraser Valley provides an EEV of 105 kg N/ha per year from ammonia. No application factor was used for this assessment, as the natural deposition rate is around 4–5 kg/ha per year and the critical load is estimated at only 10 kg/ha per year.

$$\text{Quotient} = \frac{105}{10}$$

$$= 10.5$$

Based on this quotient, there is a definite possibility that conifer forests in the Lower Fraser Valley may be detrimentally affected by ammonia deposition. Unfortunately, there is little information either on the widespread deposition of ammonia or on the effects of ammonia on Canadian terrestrial ecosystems to allow a probabilistic risk analysis to be performed.

3.1.2.2.2 Releases to water

Due to limitations of either exposure or toxicity data, the risk assessment of ammonia proceeded to a probabilistic risk assessment only for releases of ammonia from municipal WWTPs.

The LC_{10} was chosen as a short-term acute CTV because it is the maximum allowable mortality permitted in the control treatment and therefore defines the accuracy of toxicity testing. For un-ionized ammonia, the LC_{50} to rainbow trout (*O. mykiss*) for a 12-hour exposure was 0.74 mg/L, and the LC_{10} was 0.074 mg/L. The rise of ammonia in fish blood at these water concentrations is rapid. The concentration–lethality relationships are useful for estimating potential effects under these acute conditions when ammonia concentrations are very high. The conservative nature of the LC_{10} value is demonstrated by the fact that this concentration is bracketed by mortality and non-lethality in longer exposures of 21–120 days and is in the range of sublethal growth effects.

The acute lethality data for invertebrates and fish were evaluated collectively as a community of organisms by plotting the cumulative species response as a proportion of the entire community against concentrations of un-ionized ammonia (WERF, 1996). An ecological risk criterion for lethality can be derived from this distribution of data. Figure 8 is the Aquatic Community Risk Model (ACRM) graph for acute toxicity and is a logistic regression of the concentration–response. It allows prediction limits to be determined for any point on the curve. It must be remembered that each point on this graph is the average response of the species that it represents; in some cases, this is a single toxicity test, and in the case of rainbow trout (*O. mykiss*), it is an average of 112 toxicity tests. The ecological risk criterion developed is not specific to any particular water body in Canada. To conduct site-specific assessments, a review of each species' presence–absence would be required for each water body under study. This approach was beyond the scope of this assessment.

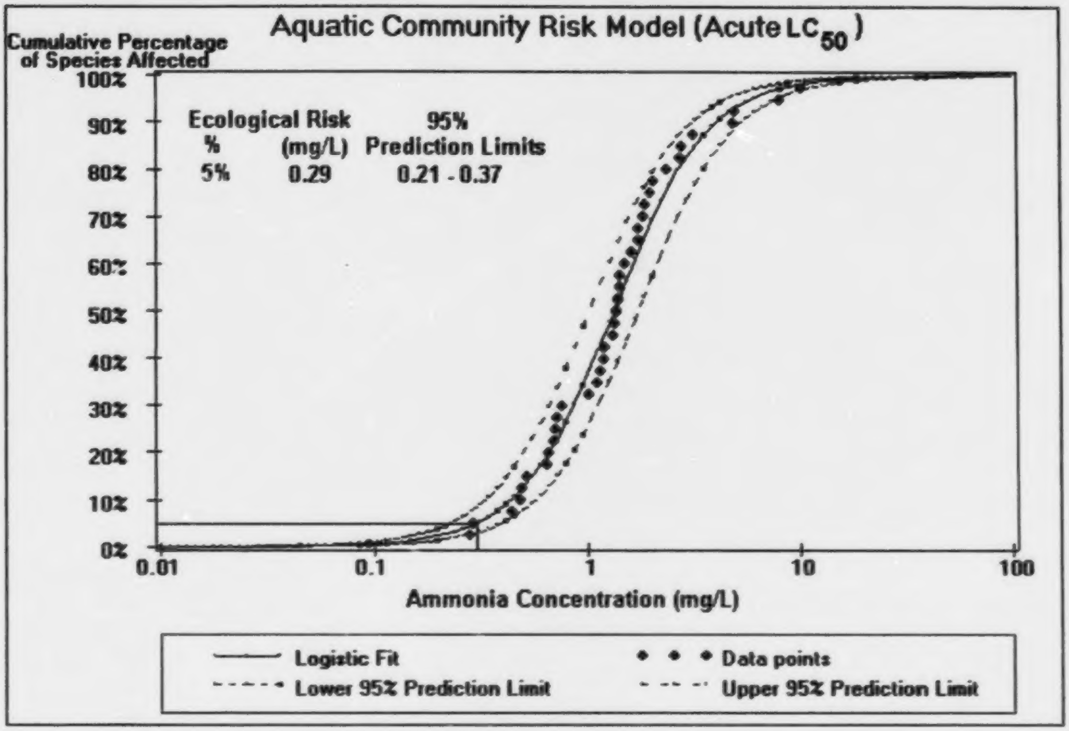

Figure 8: Acute ACRM for Canadian freshwater species

Figure 8, which uses all the LC_{50} data from Tables 4 and 5 (fish and invertebrates), indicates that 0.29 mg NH_3/L (95% prediction limits are 0.21–0.37 mg/L) would produce 50% mortality in the most sensitive organisms representing 5% of the community. It should be noted that nearly all of the measured LC_{50} values reported in the literature exceed 0.29 mg/L.

The conservative nature of these estimates is evident when considering that these values are based on constant exposure conditions over a 48- to 96-hour period, conditions that rarely occur in the field. Concentration plumes change in geographical coverage due to variable dilution and currents, and organisms can move in and out of exposure areas over that period of time as part of their natural behaviour. Few aquatic organisms are repelled by ammonia or by municipal wastewater effluents; many, in fact, will be attracted to such effluents due to their supply of organic matter and warmth.

The scientific literature on sublethal ammonia toxicity to invertebrates, amphibians and fish was reviewed in detail and in many cases reanalysed to calculate the EC_{20} (concentration causing an effect in 20% of the organisms exposed) or IC_{20} (concentration causing 20% inhibition in exposed organisms compared with the control response) (Craig, 1999). Not uncommon with growth tests is that fry mortality can be as sensitive as, if not more sensitive than, growth *per se*. The use of the EC_{20} effect concentration allows comparison of organism sensitivity using the same endpoint and avoids comparison of many different endpoints that often use different statistical methods. The use of the 20% effect level is derived from the use in sublethal bioassay tests of an allowable 20% effect in control organisms due to the difficulty in maintaining a population of organisms over a long period. As with the lethal data, the same community ecological risk criteria were developed using the acceptable sublethal data from the literature reviewed (Table 6).

Figure 9 represents the chronic ACRM graph developed for Canadian species listed in Table 6. The points on the graph are the geometric means (where they can be calculated) of the EC_{20} values for that species. The logistic regression of the community response analysis indicates that, at un-ionized ammonia concentrations above 41 µg/L (0.041 mg/L), the most sensitive 5% of the species in an exposed community would be expected to exhibit a 20% reduction in growth or reproduction. The prediction limits on this chronic CTV are 19–63 µg/L due to the relative lack of response data at the lower end of the graph. As with the acute toxicity ACRM, Figure 9 shows the average responses for each species where it was possible to calculate an average. It should also be noted (as shown in Figure 9) that all of the chronic effects values reported in the literature exceed the 0.041 mg/L value.

The acute CTV of ammonia for saltwater fish was determined to be 0.49 mg/L for the winter flounder (*P. americanus*). This is the most sensitive mean acute toxicity value reported for marine organisms (U.S. EPA, 1989).

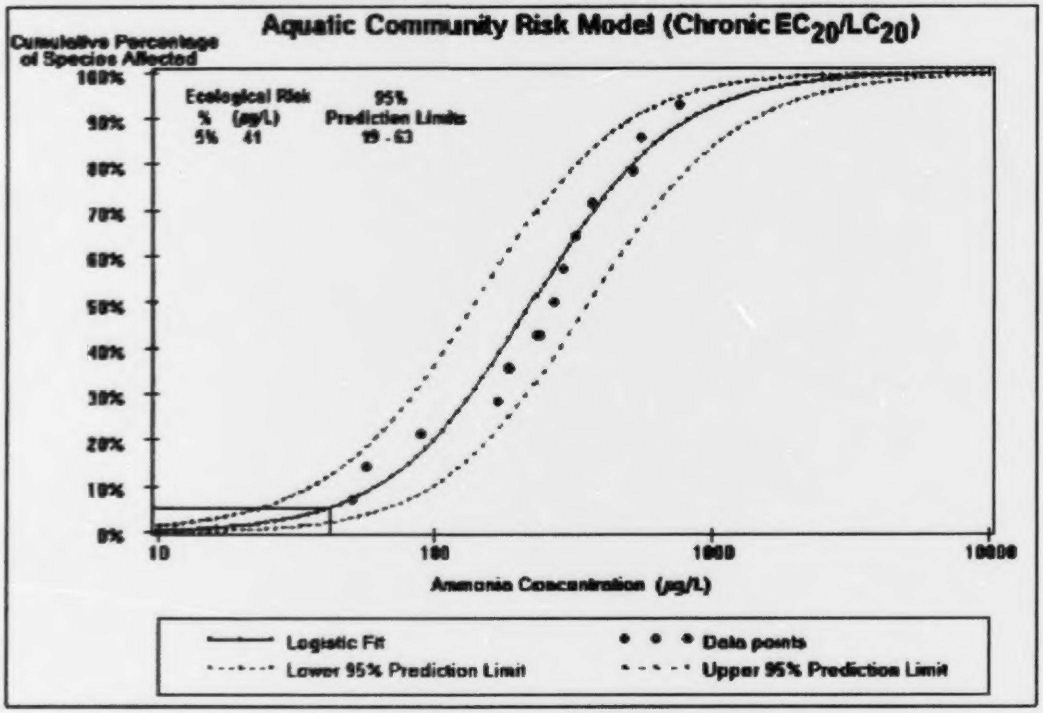

Figure 9: Chronic ACRM for Canadian species listed in Table 6

Municipal wastewater effluents

For the conservative assessment of ammonia in freshwater lakes and ocean discharges, it was decided to use un-ionized ammonia concentrations measured (a) in Hamilton Harbour, Lake Ontario, from Hamilton and Burlington municipal effluents, (b) in Lake Ontario from Toronto and (c) at the Iona Island deep-sea outfall from the Greater Vancouver Regional District. These are examples of potentially impacted lake and ocean systems (Barica, 1991; IRC Inc., 1997; Gartner Lee Ltd., 1998).

(a) Hamilton Harbour

The maximum concentration of un-ionized ammonia recorded in Hamilton Harbour in 1994 was approximately 0.35 mg/L (Charlton, 1997). This value will be used as the EEV in our lake calculations. The acute CTV of 0.29 mg NH_3/L was used. This value is close to the lowest reported acute effects levels for freshwater organisms (0.28 and 0.29 for white perch, *M. americana*, and mountain whitefish, *P. williamsoni*, respectively). An application factor of 10 was used due to the large and relatively complete database on fish toxicity.

The conservative assessment of the acute toxicity of un-ionized ammonia to fish in fresh water generated the quotient:

$$\text{Quotient} = \frac{0.35}{0.029}$$

$$= 12$$

As this quotient is over one, these concentrations could be acutely toxic to sensitive fish. The toxicity assessment of ammonia released to freshwater aquatic environments should proceed to a probabilistic risk assessment. As Environment Canada conducted a detailed water quality project in 1998, there are sufficient data to allow this assessment to be conducted (Charlton and Milne, 1999).

(b) City of Toronto

The City of Toronto discharges much of its municipal sewage effluent via a pipeline and diffuser array into Lake Ontario at Ashbridge's Bay (see Figure 10). The water is roughly 6 m deep at the diffuser array. In 1998, Environment Canada contracted Gartner Lee Ltd. to conduct an effluent sampling project around the diffuser array to determine the spread of effluent constituents, specifically chloramines and ammonia (Gartner Lee Ltd., 1998). The diffuser array was located and sampled, as well as three samples from farther out in the lake, to establish the background and range of concentrations expected. The longitudinal length of the effluent plume was determined based on maps produced in a modelling exercise, wind direction and conductivity measurements. The down-gradient extent of the effluent was defined by conductivity concentrations within 10% of the background levels.

A conservative assessment can be done for this discharge into Lake Ontario. At sites OC, 100A and 100C (top samples), the un-ionized ammonia concentrations were 0.06 mg/L or greater. The acute CTV of 0.29 mg/L was used because the organisms in this area are expected to be exposed over short periods of time, as the plume moves considerably with the wind. An application factor of 10 was used due to the relatively complete database on freshwater fish toxicity.

$$\text{Quotient} = \frac{0.06}{0.029}$$

$$= 2$$

There appears to be a slight potential for adverse effects from the Toronto Main WWTP effluents. With the uncertainty involved in this calculation and the lack of detailed information on the spatial and temporal extent of these effluents, there is not enough information to continue to a probabilistic risk assessment.

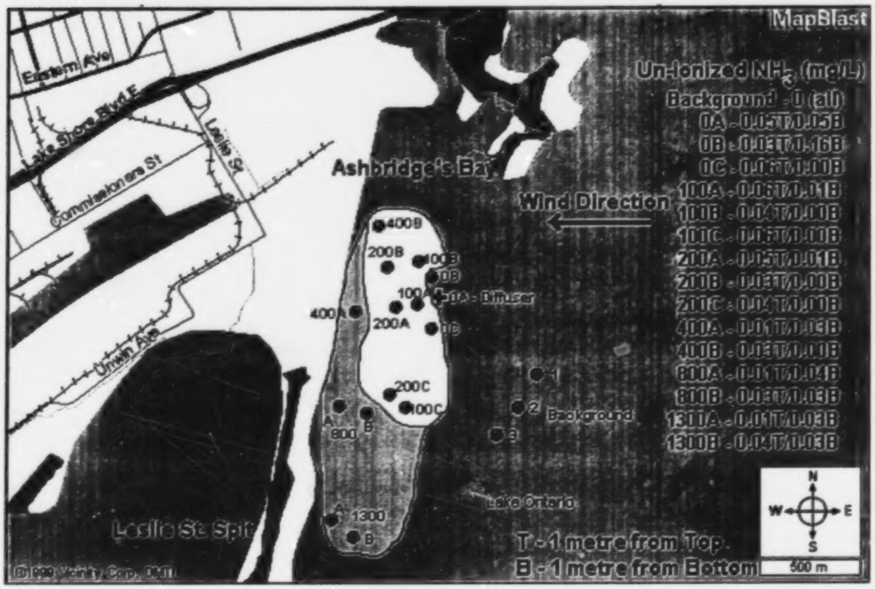
MapBlast
Un-Ionized NH_3 (mg/L)
Background - 0 (all)
0A - 0.05T/0.05B
0B - 0.03T/0.16B
0C - 0.06T/0.00B
100A - 0.06T/0.01B
100B - 0.04T/0.00B
100C - 0.06T/0.00B
200A - 0.05T/0.01B
200B - 0.03T/0.00B
200C - 0.04T/0.00B
400A - 0.01T/0.03B
400B - 0.03T/0.00B
800A - 0.01T/0.04B
800B - 0.03T/0.03B
1300A - 0.01T/0.03B
1300B - 0.04T/0.03B
Eastern Ave
Lake Shore Blvd E
Leslie St
Commissioners St
Unwin Ave
Ashbridge's Bay
Wind Direction
400B
200B
100B
0B
100A
0A - Diffuser
400A
200A
0C
200C
100C
A
B
800
1
2
3
Background
1300
Lake Ontario
Leslie St. Spit
T - 1 metre from Top
B - 1 metre from Bottom
N
W
E
S
500 m
©1999 Vicinity Corp., DMTI

Figure 10: Discharge of Toronto municipal effluent into Lake Ontario, September 1998

(c) Greater Vancouver Regional District deep-sea outfall

Opened in 1963, the Iona Island WWTP provides primary treatment of wastewater and serves the Vancouver Sewerage Area. As wastewater flows to the plant increased, environmental studies showed that the discharge of effluent across Sturgeon Bank in a shallow channel was degrading portions of the bank. Recommendations for upgrading were made and, in 1988, the Greater Vancouver Regional District commenced operation of the Iona deep-sea outfall, which replaced the previous surface discharge. The new outfall discharges treated effluent at depths ranging from about 72 to 106 m to the Strait of Georgia off Sturgeon Bank.

The plant produces a primary effluent moderately high in ammonia (10 mg/L) with a flow of 567 000 m^3/day (Environment Canada, 1997b). This facility deposits roughly 2000 tonnes ammonia/year into the Strait of Georgia. Estimates for initial dilution of the wastewater discharge indicate minimum levels in excess of 100:1 and typical levels of 150:1 at all flows and all discharge depths throughout the year.

Two years of pre-discharge data and 9 years of post-discharge data have been collected. A plume discharge study, including ammonia analyses, was conducted in 1996 following the peak Fraser River flows during a period of high-density stratification at the site. Sampling was done in July and August.

In a 1996 survey, the treated wastewater plume was detected in a north–south corridor up to 1 km north and 4 km south of the outfall diffusers either at a water depth of 55 m or at the bottom. Twenty-nine multidepth water samples were obtained at 10 sampling stations located in the area on 3 days in July 1996. There were no statistically significant differences between in-plume and outside-plume mean concentrations for ammonia in either the 55-m-depth or bottom-water samples. The maximum total ammonia concentration was 0.08 mg NH_3-N/L at 55 m depth at the diffusers, equivalent to 0.0003 mg un-ionized ammonia/L at a pH of 7.4 and a temperature of 9°C (Berthold, 1999).

A benthic survey in the vicinity of the deep-sea outfall did not detect any anomalies in the benthic or infaunal communities (Stewart *et al.*, 1991).

A concentration of 0.0003 mg un-ionized ammonia/L was detected at the Iona Island outfall, so it was used as the EEV for ocean disposal in this situation. An application factor of 10 was used due to the relative abundance of toxicity data on saltwater organisms. The acute CTV for saltwater fish (winter flounder, 0.49 mg/L) was used due to the likelihood that a benthic fish would not be exposed to the plume over long periods. Based on a maximum detected concentration of 0.08 mg NH_3-N/L (total ammonia), the conservative assessment would be:

$$\text{Quotient} = \frac{0.0003}{0.049}$$

$$= 0.006$$

Based on this high and rapid level of dilution, there does not appear to be an ecological toxicity hazard from the Iona Island deep-sea outfall.

(d) River discharges: screening

A significant point source of ammonia release to Canadian rivers is municipal WWTPs. This section examines the characteristics of effluent dilution and mixing in rivers at 10 selected municipal WWTPs across Canada. The characteristics of the effluent plumes that develop downstream of these WWTP outfalls provide insight into the spatial extent of potentially toxic zones within the river under different ambient conditions.

The model CORMIX 3.2 was selected for this application since it was suited to the variety of outfall configurations that exist and could be applied with information that was readily available (Doneker and Jirka, 1990; Jirka *et al.*, 1996; Jones *et al.*, 1996). These predictions have not been validated with field data and represent a conservative view of dilution in rivers.

Study sites were selected from across Canada that would typify the types of treatment systems and receiving environments available. The cities chosen were Edmonton, Alberta; Saskatoon, Saskatchewan; Calgary, Alberta; Winnipeg, Manitoba; Guelph, Ontario; Stratford, Ontario; Ottawa, Ontario; Montréal, Quebec; and Edmundston, New Brunswick. The cities chosen represent a mix of treatment types, discharge types and dilution rates. In each situation, average and low-flow assessments were conducted to provide reasonable estimates of the impacts from sewage treatment processes.

Table 10 summarizes the results of the modelling. In this summary, key characteristics of the plume have been identified for ease of comparison and evaluation. The CORMIX 3.2 predictions presented here are based upon average conditions in the river and assume steady flow. This is rarely the case, and therefore the actual plume locations and centre lines are expected to vary considerably with the variations inherent in rivers.

Many of the data used came from engineering drawings for each facility as presented in Walker (1998). Municipalities provided the ammonia concentrations in the effluents; the water temperatures at average and low flows were estimated for most locations. By assuming a constant pH of 8 for all of the rivers and flow conditions, the un-ionized ammonia concentration was estimated. The point at which the toxicity estimate was made is the 10:1 dilution point, as modelled by CORMIX. The chronic CTV of 0.041 mg/L was used without an application factor. From this, a conservative estimate can be made of the potential for a chronic impact from ammonia for each outfall.

Table 10: Summary of conservative assessment of modelled sewage treatment systems[1]

Location	Total NH_3 (at 10:1 dilution)	Flow	Temperature (°C)	EEV as un-ionized NH_3 (mg/L)	Distance to 10:1 dilution (m)	Season	Toxicity quotient
Edmonton	2.142	Low	4	0.024	10 000	winter	0.6
		Avg.	24	0.106	1 935	summer	2.7
Calgary	0.5	Low	4	0.006	>55 000	winter	0.2
		Avg.	17	0.015	13 000	summer	0.4
Saskatoon	1.178	Low	4	0.013	111	winter	0.3
		Avg.	23	0.055	7	summer	1.4
Winnipeg N	1.865	Low	4	0.021	3 400	winter	0.5
		Avg.	23	0.087	150	summer	2.2
Winnipeg W	0.878	Low	25	0.047	>20 000	summer	1.2
		Avg.	15	0.023	94	spring–fall	0.6
Ottawa	0.608	Low	25	0.032	<1	summer	0.8
		Avg.	15	0.016	<1	fall	0.4
Stratford	1.257	Low	28	0.081	>1 500	summer	2.0
		Avg.	10	0.023	>1 500	fall	0.6
Guelph	0.239	Low	28	0.015	Not achieved	summer	0.4
		Avg.	10	0.004	2 120	fall	0.1
Montréal	0.659	Low	22	0.029	660	summer	0.7
		Avg.	10	0.012	830	fall	0.3
Edmundston	1.667	Low	22	0.072	22	summer	1.8
		Avg.	10	0.030	3 000	fall	0.8

[1] Discharges highlighted are not significant.

This exercise indicates that ammonia in sewage effluents from some cities is likely toxic under some conditions, but not under others. The cities of Edmonton, Winnipeg (North and West End plants), Edmundston and Stratford all have potentially toxic plumes of a significant size, under some conditions. Edmonton and Winnipeg generate potentially toxic plumes of a significant size under average conditions simulated. There are sufficient data on the effluents from both of these cities and their rivers to conduct probabilistic risk assessments. Because of the very long distance to the 10:1 dilution point below Calgary (>56 km), there is the possibility of "toxic" conditions prior to this point.

The cities of Saskatoon, Guelph, Ottawa-Carleton and Montréal do not have potentially toxic effluents under the situations simulated here. This is due to ammonia removal processes on the part of Guelph and to ammonia reduction techniques and a wide diffuser in the Ottawa River on the part of Ottawa-Carleton and in the South Saskatchewan River on the part of Saskatoon. Montréal has a weak effluent for a primary treatment system (6 mg/L) and a large dilution capacity in the St. Lawrence River.

Since this work was completed, the cities of Saskatoon and Stratford have installed nitrification systems to remove or alter the form of ammonia they are putting into their local rivers, and they no longer release ammonia concentrations that are toxic under any conditions.

Table 10: Summary of conservative assessment of modelled sewage treatment systems[1]

Location	Total NH_3 (at 10:1 dilution)	Flow	Temperature (°C)	EEV as un-ionized NH_3 (mg/L)	Distance to 10:1 dilution (m)	Season	Toxicity quotient
Edmonton	2.142	Low	4	0.024	10 000	winter	0.6
		Avg.	24	0.106	1 935	summer	2.7
Calgary	0.5	Low	4	0.006	>55 000	winter	0.2
		Avg.	17	0.015	13 000	summer	0.4
Saskatoon	**1.178**	**Low**	**4**	**0.013**	**111**	**winter**	**0.3**
		Avg.	**23**	**0.055**	**7**	**summer**	**1.4**
Winnipeg N	1.865	**Low**	**4**	**0.021**	**3 400**	**winter**	**0.5**
		Avg.	23	0.087	150	summer	2.2
Winnipeg W	0.878	Low	25	0.047	>20 000	summer	1.2
		Avg.	**15**	**0.023**	**94**	**spring–fall**	**0.6**
Ottawa	**0.608**	**Low**	**25**	**0.032**	**<1**	**summer**	**0.8**
		Avg.	**15**	**0.016**	**<1**	**fall**	**0.4**
Stratford	1.257	Low	28	0.081	>1 500	summer	2.0
		Avg.	**10**	**0.023**	**>1 500**	**fall**	**0.6**
Guelph	**0.239**	**Low**	**28**	**0.015**	**Not achieved**	**summer**	**0.4**
		Avg.	**10**	**0.004**	**2 120**	**fall**	**0.1**
Montréal	**0.659**	**Low**	**22**	**0.029**	**660**	**summer**	**0.7**
		Avg.	**10**	**0.012**	**830**	**fall**	**0.3**
Edmundston	1.667	**Low**	**22**	**0.072**	**22**	**summer**	**1.8**
		Avg.	10	0.030	3 000	fall	0.8

[1] Discharges highlighted are not significant.

This exercise indicates that ammonia in sewage effluents from some cities is likely toxic under some conditions, but not under others. The cities of Edmonton, Winnipeg (North and West End plants), Edmundston and Stratford all have potentially toxic plumes of a significant size, under some conditions. Edmonton and Winnipeg generate potentially toxic plumes of a significant size under average conditions simulated. There are sufficient data on the effluents from both of these cities and their rivers to conduct probabilistic risk assessments. Because of the very long distance to the 10:1 dilution point below Calgary (>56 km), there is the possibility of "toxic" conditions prior to this point.

The cities of Saskatoon, Guelph, Ottawa-Carleton and Montréal do not have potentially toxic effluents under the situations simulated here. This is due to ammonia removal processes on the part of Guelph and to ammonia reduction techniques and a wide diffuser in the Ottawa River on the part of Ottawa-Carleton and in the South Saskatchewan River on the part of Saskatoon. Montréal has a weak effluent for a primary treatment system (6 mg/L) and a large dilution capacity in the St. Lawrence River.

Since this work was completed, the cities of Saskatoon and Stratford have installed nitrification systems to remove or alter the form of ammonia they are putting into their local rivers, and they no longer release ammonia concentrations that are toxic under any conditions.

Agricultural runoff

There is no single assessment possible that would cover the many ways in which ammonia could be emitted from an agricultural operation due to the wide variety of such operations across Canada. Therefore, a series of conservative assessments have been conducted for those typical operations where there are data. The results are presented in Table 11.

Application factors of 10 have been used due to the relatively complete database on freshwater fish. In these cases, EEVs have been used from a variety of agricultural situations (see Table 11). Impacts from allowing cattle free access to a small river can be estimated based on Demal (1983) and his study of cattle in the Avon River, Ontario. This is one of the few studies found that estimates ammonia from this source. The short- and long-term impacts from cattle overwintering along a stream can be estimated from the studies by Cooke (1996) and Anderson *et al.* (1998a), respectively. Both of these studies were conducted in Alberta, where beef cattle are common; no other studies could be found pertaining to eastern Canadian situations. The impacts of ammonia in runoff from winter-applied manure can be estimated from Green (1996). The concentrations used in all of these assessments were the maximum detected.

Table 11: Summary of conservative assessments for agricultural runoff situations

Situation	Conditions of entry to water	EEV (mg un-ionized ammonia/ L)	CTV (mg/L)	Application factor	ENEV (mg/L)	Quotient
Cattle crossing a stream	Temp. 19°C, pH 7.7, slow water	0.008	0.29 (acute)	10	0.029	0.3
Cow-calf operations – long term	Temp. 11.5°C, pH 7.5, spring to fall	0.022	0.04 (chronic)	10	0.004	6
Cow-calf operations – short term	Temp. 1°C, pH 7.05, spring	0.04	0.29 (acute)	10	0.029	1.4
Feedlot/dairy runoff	Temp. 1°C, pH 7.05, spring	0.13	0.29 (acute)	10	0.029	4.5
Manure fertilization runoff	Temp. 2°C, pH 7.8, manure applied to snow; local river sampled	0.003	0.29 (acute)	10	0.029	0.1
Manure fertilization runoff	Temp. 2°C, pH 7.8, manure applied to snow; max. NH_3 in ditch	0.116	0.29 (acute)	10	0.029	4

Conservative analyses of agricultural operations with minimal data that involve cattle and manure handling have shown that some practices (overwintering cow-calf operations near streams, long-term cow-calf operations near streams, feedlot/dairy runoff near streams in springtime, manure fertilization of snow-covered fields near streams) have the potential to cause acute toxicity to aquatic organisms. Unfortunately, there is insufficient information on these types of agricultural systems across Canada to allow this analysis to be continued to a level that would include an assessment of the probability of adverse effects.

Dredged saltwater sediments

Concentrations of ammonia in sediment pore water in dredged material from estuarine and marine sites have been reported by the U.S. Army Corps of Engineers (Gibson *et al.*, 1995) and in the open literature (Sims and Moore, 1995). U.S. data were used since Canadian data were limited. Approximately 21 of the sites were estuarine (salinity = 1–30‰), 5 were marine (salinity > 30‰) and 13 were fresh water (salinity <1‰). Where concentrations were represented as total ammonia, un-ionized ammonia was calculated from reported pH, salinity and temperature. When the necessary parameters were not available, the following values were assumed: pH = 7.5, temperature = 20°C and salinity = 20‰ for estuarine systems and 30‰ for marine systems. Conversions were based on the results of a study conducted by Hampson (1977). In general, the median pore water ammonia concentration reported in the dredged material survey was 0.2 mg NH_3/L. Pore water ammonia concentrations for estuarine sites ranged from 0.06 to 1.9 mg NH_3/L. Due to the suspension of sediments in the water column through which the sediment falls, a dilution factor of 10 was applied to the reported EEVs.

The receptor organism is winter flounder (*P. americanus*), which exhibits an average LC_{50} of 0.49 mg/L. An acute CTV is used, as exposure to ammonia from dumping sediments is expected to be of short duration. An application factor of 10 was used due to the relatively complete database on saltwater toxicity to convert this CTV to an ENEV of 0.049 mg/L.

Data available in the published literature for estuarine and marine conditions presented a range of exposure values for ammonia concentration in sediment pore water. Due to the variation in exposure values among sampling sites, risk quotients were calculated using the median and maximum concentrations from the dredged material survey, 0.2 and 1.9 mg NH_3/L, respectively. The assumed pH of 7.5 is too low and the temperature of 20°C is too high for Canadian marine waters (Berthold, 1999), so the average ammonia concentration was recalculated using a pH of 7.8 and a temperature of 9°C. Using the methodology of Spotte and Adams (1983) to calculate a ratio between NH_4^+ and NH_3 in saline water, the median ammonia concentration would be 0.12 mg/L and the maximum would be 1.18 mg/L. Because of the dilution effect that will occur as the dredged sediments fall through the water column, an estimated dilution factor of 10 was applied.

Median

$$\text{Quotient} = \frac{0.012}{0.049}$$

$$= 0.24$$

Maximum

$$\text{Quotient} = \frac{0.118}{0.049}$$

$$= 2.4$$

Using this method, the acute risk quotients for dredging and dumping ammonia-laden material in a saltwater environment would be <1 using a median concentration of 0.12 mg NH_3/L and >1 using the maximum concentration of 1.18 mg/L from dredging surveys done in the United States. The results suggest that the risk of pore water ammonia toxicity in dredged material bioassays is highly variable and depends on the scenario and assumptions considered. The exposure period used to generate the CTV does not adequately match the exposure in the environment, as winter flounder was exposed for 96 hours. It is highly unlikely that benthic fish would be exposed for this time period from dredging operations. Also, the dilution factor of 10 has not been validated, and the physical parameters of saline water (temperature, pH and salinity) can have a major effect on un-ionized ammonia concentrations.

Ammonia is also a natural constituent of sediment. In published literature, a concentration range of 0.17–17 mg un-ionized ammonia/L in sediment pore water was reported to be quite common, and concentrations as high as 430 mg/L have also been reported (Gibson *et al*., 1995). Calculation of risk quotients using some naturally occurring ammonia concentrations would result in a quotient greater than one.

The conservative assessment of dredged sediments suggests that sensitive pelagic organisms might be harmed by exposure to ammonia liberated from sediments during dredging and dumping, but considerably more work would have to be done to prove that this source of ammonia is harmful in marine environments.

3.1.2.2.3 Other lines of evidence

Ammonia concentrations in interstitial pore waters of sediments are frequently of concern when dredging is to be carried out on the sediments (Schubauer-Berigan and Ankley, 1991). Dredging sediment high in ammonia can liberate considerable concentrations of ammonia to the surrounding water, and redepositing the sediment can also create a hazard. Dredged sediment disposal has been shown to cause toxicity in surrounding waters to *Daphnia* sp., *Polydora* sp. and *Paleomonetes* sp. by DeCoursey and Vernberg (1975). Although these researchers did not take water samples for analysis of ammonia, samples were taken from similar operations in the area. These samples contained up to 5 mg NH_3/L at a sediment disposal site and 0.123 mg/L in non-disposal areas.

A major effluent sampling, characterization and effects project was carried out in 1993–1994, called the Joint Industrial–Municipal North Saskatchewan River Study (Golder Associates, 1995). A map of the North Saskatchewan River is illustrated in Figure 11. The project characterized the extent of the effluent plume from the Edmonton WWTP and from a smaller WWTP 20 km downstream. This project formed the basis for most of the plume-specific information used to model the effluent plume for the probabilistic risk analysis on this source. This project also characterized the nature of the benthic invertebrate community above and below the Edmonton WWTP outfall.

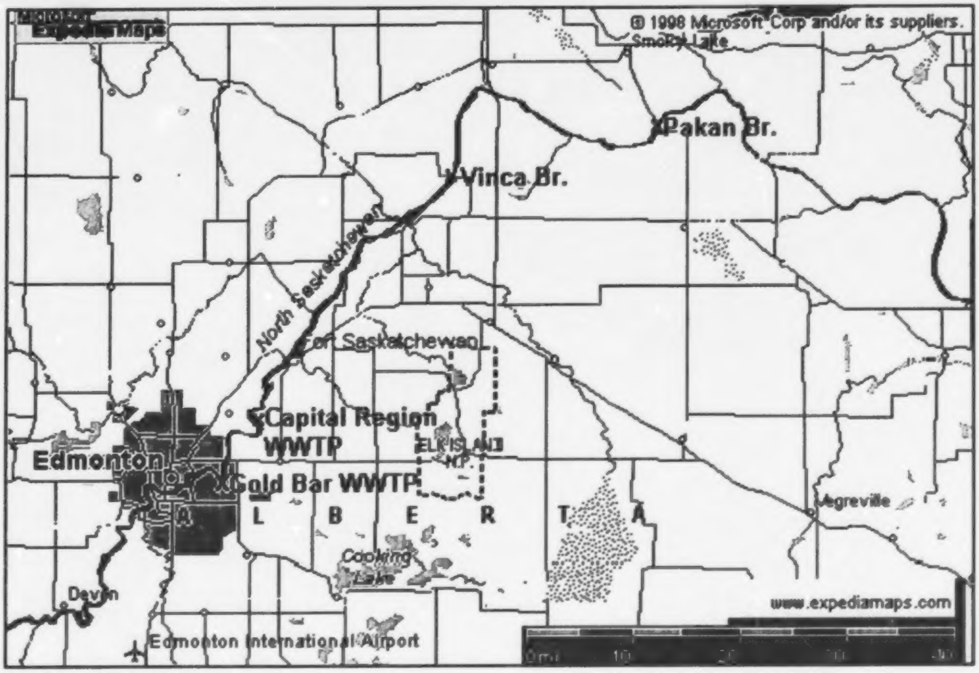
Expedia Maps
© 1998 Microsoft Corp and/or its suppliers.
Smoky Lake
Pakan Br.
Vinca Br.
North Saskatchewan
Fort Saskatchewan
Capital Region WWTP
Edmonton
Gold Bar WWTP
ELK ISLAND N.P.
A L B E R T A
Vegreville
Cooking Lake
Devon
Edmonton International Airport
www.expediamaps.com
0 mi
10
20
30
40

Figure 11: North Saskatchewan River in the vicinity of Edmonton

Total numbers of invertebrates and taxonomic richness are well-established indicators of environmental quality in rivers. Coupled with the coarse-level taxonomic breakdown of the data, these variables are sufficient to identify the major factor influencing the benthic community of a river. The longitudinal pattern in invertebrate abundance and community composition in the study reach is largely indicative of nutrient enrichment contributed by WWTPs (Golder Associates, 1995). Sewage effluents from Edmonton have altered the zoobenthic community below the discharge from an assembly of clean-water taxa (dominated by species of stoneflies, mayflies and caddisflies) to a less diverse and more abundant fauna characterized by pollution-tolerant taxa (such as oligochaetes and chironomids) (Anderson *et al.*, 1986). Direct effects from nutrients were evident in increased plant growth (measured as chlorophyll *a*), whereas secondary and synergistic effects contributed to some decrease in dissolved oxygen levels, some increase in biochemical oxygen demand, and cyclic and compositional changes in the zoobenthic community (Anderson *et al.*, 1986).

Dissolved oxygen in the river is always high, with only a slight oxygen sag below the Edmonton discharge. This usually amounts to a 5% decrease in the percent saturation from 75% to 70% in July (equivalent to 5.5 mg/L at the time). Farther downstream from Gold Bar, the dissolved oxygen, as percent saturation, increases from 70% to >80%. A value of 60% saturation would protect natural populations of all organisms in the North Saskatchewan River (Anderson *et al.*, 1986).

Benthic invertebrate monitoring of the North Saskatchewan River downstream from municipal and industrial outfalls downstream of Edmonton documented severe benthic community alteration. The large increase in oligochaetes (Tubificidae and Naididae) below the Gold Bar WWTP followed by chironomid (Chironomini, Orthocladiniinae, Tanytarsini and Tanypodinae) dominance are typical effects of strong nutrient enrichment. A substantial increase in the abundance of pollution-tolerant oligochaete worms generally occurs in this zone at the expense of sensitive taxa. Farther downstream, the large increase in benthic algal biomass resulting from increased nutrient level results in chironomid dominance, followed by a gradual return of more sensitive invertebrates. Moderately enriched far-field areas may support dense populations of chironomids, net-spinning caddisfly larvae and certain mayfly nymphs. Stonefly nymphs (Plecoptera, Chloroperlidae and Perlodidae) generally recover the farthest from WWTP outfalls. The abundance of these invertebrates did not return to upstream levels within 65 km of the study area. Water boatmen (Callicorixa) became abundant in areas with extensive growths of attached macrophytes below the outfall that provided good habitat (Golder Associates, 1995).

Lakes in the Central Plains of southern Alberta, Saskatchewan and Manitoba lie in fertile soils that supply high concentrations of nutrients. Eutrophication is generally the single most important water quality issue (Government of Canada, 1996; Hall *et al.*, 1999).

The Qu'Appelle Valley extends over 400 km from its headwaters near Lake Diefenbaker in western Saskatchewan to its confluence with the Assiniboine River in western Manitoba. The Qu'Appelle River and its tributaries provide water to approximately one-third of Saskatchewan's population, including the cities of Regina and Moose Jaw. Agricultural fields and pastures comprise more than 95% of land use in the drainage basin (Hall *et al.*, 1999). A chain of eight lakes, including two headwater reservoirs and six natural lakes, forms a gradient of trophic status in the valley. These lakes represent a major recreational and economically valuable resource for southern Saskatchewan. They are used for commercial and game fishing, recreation, irrigation, livestock watering, drinking water supply and sewage discharge, in addition to serving as flood control and waterfowl habitat (Munroe, 1986; Chambers, 1989).

Typical of the prairies, the lakes are shallow and hypereutrophic (total phosphorus >300 µg/L) and produce immense blooms of blue-green algae throughout the summer (Munroe, 1986; Kenney, 1990; Hall *et al.*, 1999). Although the lakes are naturally eutrophic, present water quality is considerably worse than before European settlement and intensive agricultural development of the region (Allan *et al.*, 1980; Hall *et al.*, 1999). Growing concern over the continued deterioration of water quality in the Qu'Appelle Lakes in the last 30 years resulted in several federal–provincial studies, which attributed excessive algal and plant growth to high nutrient concentrations in agricultural runoff and municipal sewage discharge. It was estimated that 70% of the phosphorus and nitrogen entering the river basin was from sewage discharged by Regina and Moose Jaw (Munroe, 1986). Regina upgraded its sewage treatment facility to remove phosphorus in 1976, and Moose Jaw diverted all of its sewage to agricultural land through the use of spray irrigation by 1987 (Chambers, 1989).

It is unclear whether the upgrades to the sewage treatment plants have had the desired effect on water quality in the Qu'Appelle Lakes. Although open-water total phosphorus concentrations in the lakes have decreased despite increased annual discharge (Chambers, 1989), recent paleolimnological analysis indicates that nitrogen loading to the Qu'Appelle Lakes is at an all-time maximum (Hall *et al.*, 1999). Similarly, the outflow of the Fishing Lakes exhibits an extremely low ratio of total nitrogen to total phosphorus (2.6:1), which suggests that phosphorus is being retained in the lakes, probably in the sediments. This situation maximizes primary production (Munroe, 1986). This evidence suggests that primary production in the Qu'Appelle Lakes would be nitrogen, not phosphorus, limited. Water quality is, thus, not likely to improve until nitrogen removal technology is instituted at Regina's WWTP or until the phosphorus pool in the sediments is depleted.

3.1.2.3 Probabilistic risk assessment

Ecological risk assessment for ammonia using the conservative quotient method indicated that sewage effluents are a major source of toxicity to aquatic habitats. The results identified three case studies where a probabilistic risk assessment could be conducted due to the relative completeness of the data and the likelihood of negative impacts. These are:

1. Hamilton Harbour,
2. the North Saskatchewan River downstream of the Gold Bar municipal WWTP, and
3. the Red River downstream of Winnipeg's three municipal WWTPs.

These case studies are fairly typical of municipal wastewater discharges in Canada. Two are located on fairly large, yet slow rivers supporting large urban populations, while the other is a lake discharge situation with minimal water exchange and intensive urban development in the surrounding watershed. Considering that no two municipal wastewater discharge situations are the same, these case studies should provide a good, generic probabilistic risk assessment for this source of ammonia to fresh water.

3.1.2.3.1 Hamilton Harbour

Extensive sampling was done in 1998 (Charlton and Milne, 1999) to complement measurements taken routinely at a station in the centre of the harbour. The crosses on Figure 12 show the sewage outfall locations in Hamilton Harbour.

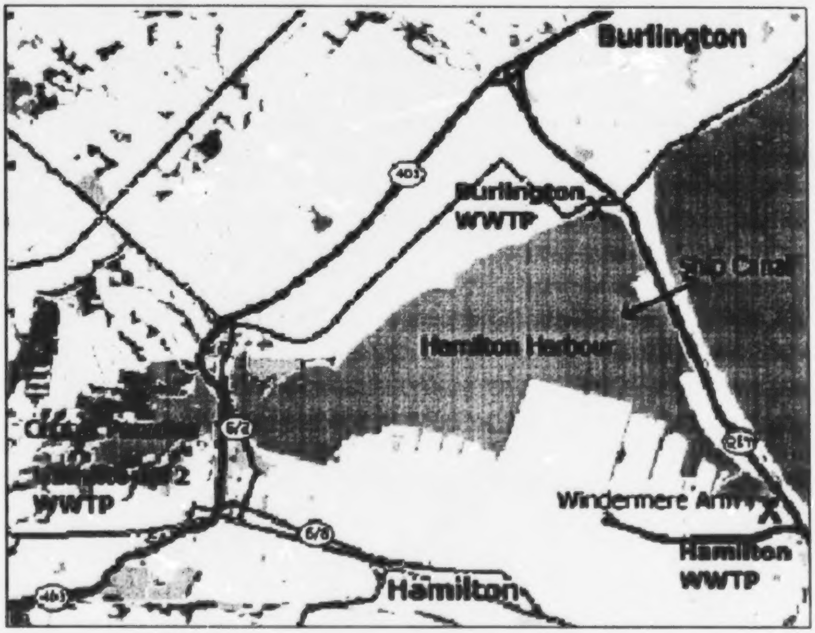

Figure 12: Hamilton Harbour

Figure 13 illustrates seasonal fluctuations in ammonia concentrations at the central station in Hamilton Harbour for the years 1986–1999. Weekly grab samples were collected for these years. For the last 6 years, the peak ammonia concentration found in early spring has been increasing. The rapid decrease of ammonia in late spring and summer is caused by nitrifying bacteria that produce nitrate from total ammonia. The nitrifying process is greatly reduced in the winter due to the sensitivity of the bacterial community to low temperatures. As a result, ammonia accumulates in the water during the winter.

As the nitrification process begins to consume ammonia in the spring due to warming temperatures, the proportion of un-ionized ammonia increases for the same reason. At the same time, increasing algal growth withdraws carbon dioxide from the water, and this causes the pH to rise, which also causes the proportion of un-ionized ammonia to increase. The net result is that the timing of the temperature and pH cycle produces increasing concentrations of un-ionized ammonia, even though the total concentration is decreasing in spring (Charlton and Milne, 1999).

The peak ammonia concentration therefore occurs in the spring and depends on the loading rate of ammonia (Rodgers *et al.*, 1992). However, in 1997–1998, several unusual occurrences generated lower than usual ammonia concentrations in the harbour (the concentration was lower by about 0.4 mg/L). The winter of 1998 was unusually mild and the spring was relatively warm, resulting in slightly higher bacterial nitrification, which degraded some of the ammonia. The load from the Woodward sewage treatment plant, which is the main source of ammonia to the harbour, was lower in the fall and winter of 1997–1998. In addition, the ammonia load from the Burlington Skyway sewage plant was lower than normal the previous winter during interruption of operations at a local food processing plant. Thus, both higher temperature and lower ammonia load explain the lower than usual ammonia concentrations in 1998 (Charlton and Milne, 1999) (Figure 13).

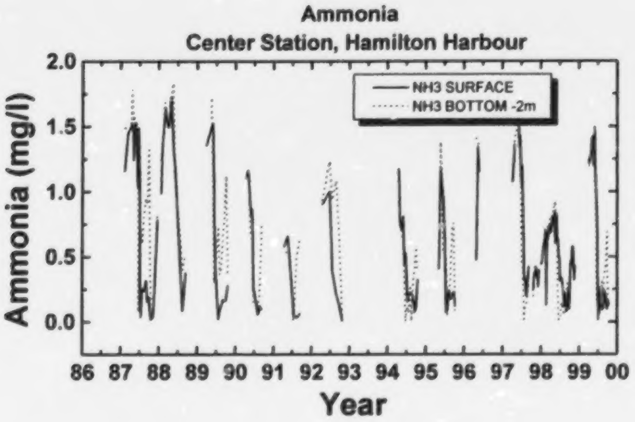

Figure 13: Seasonal fluctuations in ammonia (mg/L) at the central station in Hamilton Harbour

Un-ionized ammonia concentrations were usually much higher in the Windermere Arm than elsewhere in the harbour (see Figure 12 for location). The Windermere Arm receives water discharging from the Windermere Basin at the southeast end of the harbour. The Woodward Avenue sewage treatment plant discharges into Redhill Creek near the upstream opening into Windermere Basin. The outflow from the basin comprises mostly treated sewage, along with creek water and combined sewer overflows. The sewage treatment plant is the major source of ammonia in the basin outflow (Charlton and Milne, 1999).

The data at the central station represented the overall condition of the harbour reasonably well. Even though the central station data were not always the same as the harbour mean, they lay partway between the extremes of the data. The main ammonia loads occur in shallow water near shore, so that those waters will generally have more severe ammonia conditions than will the centre of the harbour. In the centre, the harbour is about 25 m deep at the deepest point. During the spring and summer, the surface water warms, but the rate of warming is less in the lower water, causing a bilayer system to form, because the cool, lower layer is denser. Analyses of water samples collected at 1, 3, 5, 7 and 19 m at the central station show that, until mid-May, ammonia concentrations at all the depths were similar. With the warming in May, concentrations began to decline, but the lower, cooler depths declined the fastest. This seems paradoxical, because the nitrification rate is dependent on temperature. The cause of the rapidly declining ammonia concentrations in the bottom layer is a deep-water flow that brings lake water into the bottom of the harbour via the shipping canal. This dilutes and displaces some of the ammonia accumulated during winter. The bottom water at this time is a potential refuge for fish from high un-ionized ammonia concentrations. The relatively low temperature in the bottom water also favours the ionized form of ammonia. By the end of June, however, the dissolved oxygen in the bottom water is near zero, and this excludes fish and most other higher organisms. Thus, there is no real escape from high un-ionized ammonia in the surface water (Charlton and Milne, 1999).

Exposure concentrations for ammonia were developed from the collection and analysis of water samples from Hamilton Harbour. Two sampling locations were selected: (1) Windermere Arm, where ammonia concentrations are typically the highest in the harbour, and (2) a central station where ammonia concentrations are representative of the overall conditions in the harbour (Figure 12).

Sixty-eight samples were collected from Windermere Arm between March 31 and August 31, 1998 (Charlton and Milne, 1999). Concentrations of un-ionized ammonia ranged from 0.003 to 0.63 mg/L. At the central station, 21 samples were collected at a depth of 1 m between January and September 17, 1998. Concentrations of un-ionized ammonia are represented in Figure 14; concentrations ranged from ≤0.01 to 0.11 mg/L.

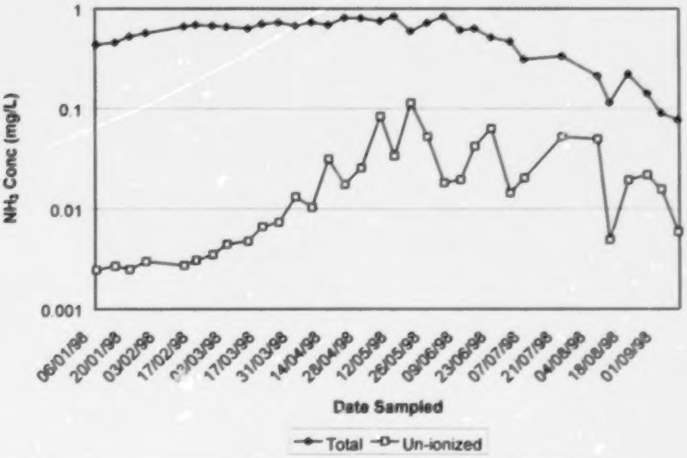

Figure 14: Total and un-ionized ammonia concentrations at the central station in Hamilton Harbour, 1-m depth

Due to the relatively high ammonia concentrations and length of exposures to ammonia in Hamilton Harbour, ecological risks were determined in three ways. The short-term acute CTV was used for a risk assessment of rainbow trout (*O. mykiss*) passing through Windermere Arm over a short period of time; the acute CTV was used to assess lethality risk to organisms in the harbour exposed to intermittent elevated concentrations. The chronic CTV was used to assess the risk in the harbour from exposure to long-term average concentrations. Craig (1999) analysed published trout toxicity data for short-term exposure to high ammonia concentrations. For un-ionized ammonia, the LC_{50} for a 12-hour exposure was 0.74 mg/L, and the LC_{10} was 0.074 mg/L.

Craig (1999) also analysed ammonia LC_{50} data using the Water Environment Research Foundation (WERF, 1996) methodology for logistic regression analysis of community toxicity data. A concentration of 0.29 mg NH_3/L would, on average, theoretically produce 50% mortality in the most sensitive organisms representing the 5th percentile of the aquatic community. This value is approximately equal to the lowest acute effect level for freshwater species that was found in the published literature.

Ammonia sublethal toxicity data were analysed using the WERF regression analysis approach. At un-ionized ammonia concentrations above 0.041 mg/L, 5% of the species in an exposed community would exhibit a 20% reduction in growth or reproduction. This value is also just below the lowest reported chronic effect level for freshwater species (Table 6).

Figure 15 presents the risk analysis for ammonia in Windermere Arm, Hamilton Harbour. Of the weekly ammonia samples taken from Windermere Arm in 1998, there was a slight chance (<4%) that un-ionized ammonia concentrations could exceed the acute CTV of 0.29 mg/L (96-hour LC_{50}). The ammonia concentrations never reached that high a level in the rest of the harbour. Eighteen percent of samples contained un-ionized ammonia concentrations exceeding the short-term acute CTV for trout (12-hour LC_{10}) of 0.074 mg/L. Forty-five percent exceeded the chronic CTV (EC_{20} growth/reproduction) of 0.041 mg/L (Figure 15).

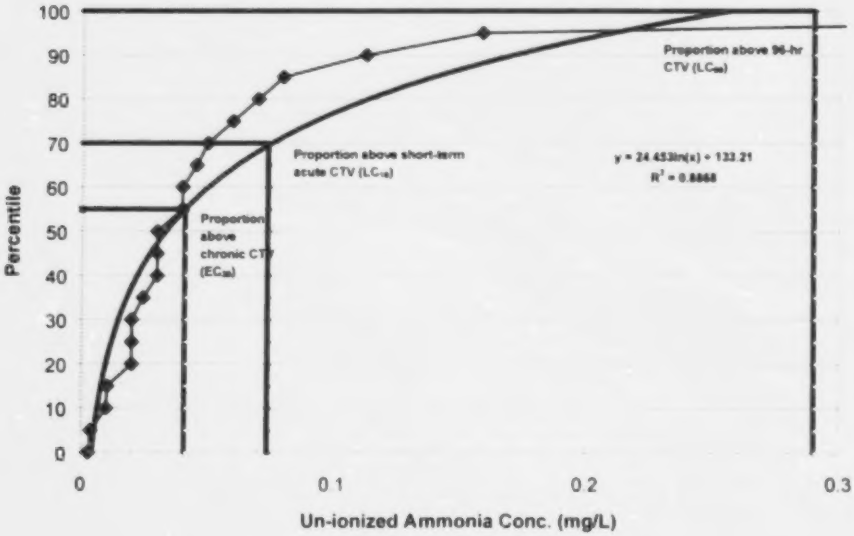

Figure 15: Un-ionized ammonia concentrations in Windermere Arm, Hamilton Harbour

This analysis assumes that weekly samples approximate 96-hour average ammonia concentrations and that the logarithmic trend line in Figure 15 approximates the actual percentile of time that fish are exposed up to a concentration ($R^2 = 0.89$). It indicates that in Windermere

Arm, there is little probability that ammonia concentrations would be lethal to 50% of sensitive fish species that remained in the Arm for 96 hours. However, 30% of the time, ammonia concentrations would be expected to cause 10% mortality in a population of rainbow trout passing through the Arm over a 12-hour period. Forty-five percent of the time, the concentrations of un-ionized ammonia in the Arm would be expected to cause a 20% reduction in growth or reproduction in the most sensitive organisms present in the Arm for an extended period of time.

Because the conditions at the central sampling site in Hamilton Harbour were sufficiently similar to those of other stations around the harbour (Charlton and Milne, 1999), this site was used to estimate effects from ammonia in the rest of the harbour. Again, the analysis assumes that sampling times approximate the test exposures and that the logarithmic trend line in Figure 16 approximates the actual percentile of time that fish are exposed up to a concentration ($R^2 = 0.95$). The conditions in the rest of Hamilton Harbour were not as severe as in Windermere Arm. None of the samples reached the 96-hour acute CTV of 0.29 mg/L. However, Figure 16 illustrates that 8% of samples contained un-ionized ammonia concentrations exceeding the short-term acute CTV for trout (LC_{10}, 0.074 mg/L) and 36% exceeded the chronic CTV (EC_{20}, 0.041 mg/L).

This means that in Hamilton Harbour, 8% of the time un-ionized ammonia concentrations would be expected to cause 10% mortality in a population of rainbow trout resident for at least 12 hours and 36% of the time un-ionized ammonia in the harbour would cause a 20% reduction in growth or reproduction of the most sensitive group of species in the harbour.

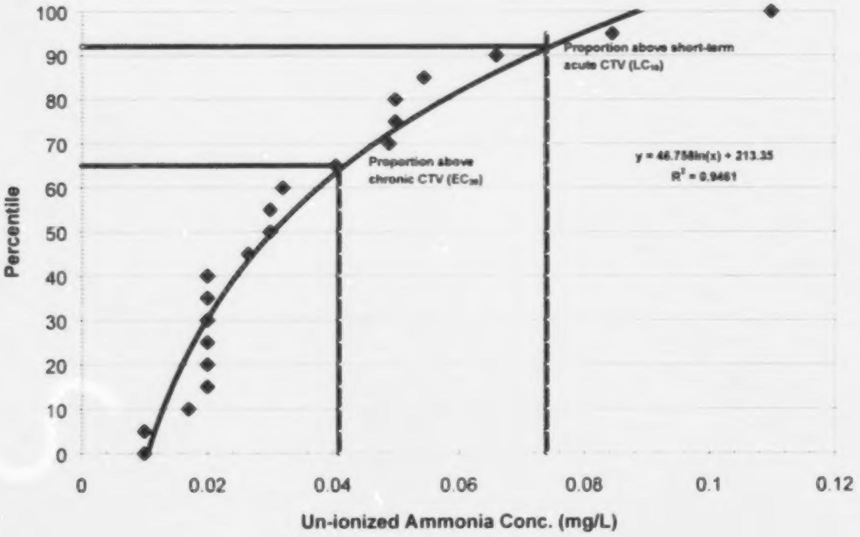

Figure 16: Risk curve for un-ionized ammonia at the central station in Hamilton Harbour

In summary, in 1998, many sites in Hamilton Harbour had concentrations of un-ionized ammonia that were up to 0.11 mg/L. Un-ionized ammonia concentrations in other areas were above concentrations that are generally safe for aquatic organisms. The ammonia concentrations in 1998 were unusually low. The central harbour site is reasonably similar to the rest of the harbour and, if anything, underestimates ammonia concentrations in shallow-water areas (Charlton and Milne, 1999).

It is concluded that un-ionized ammonia concentrations in the central station of Hamilton Harbour and in Windermere Arm are sufficiently high to cause significant adverse sublethal effects on sensitive organisms that could normally be expected to inhabit these areas. For short periods, the concentrations of un-ionized ammonia can be expected to be acutely lethal to a portion of the rainbow trout population in the harbour.

3.1.2.3.2 North Saskatchewan River

Direct measurements of ammonia in the North Saskatchewan River showed that there is a zone of potential toxicity generated in the river downstream from the City of Edmonton's sewage effluents. The data for this study were collected at only one period of time (September 1993), although they were collected over a large reach of the river. While useful for a validation for the CORMIX plume dispersion modelling program, this study could not be used to adequately determine the risk to aquatic organisms.

An evaluation of the field monitoring data for the North Saskatchewan River revealed that the data were insufficient to enable development of an exposure cumulative density function (CDF). As an alternative, the CORMIX model was used to estimate levels of un-ionized ammonia at various distances downstream of the WWTP. Initial analyses with CORMIX indicated that ammonia levels in the North Saskatchewan River are typically highest in August. Therefore, the assessment was focused on this month to estimate exposure and risks. Because CORMIX is not a distributional model, exposure CDFs were developed. The steps are described in Appendix D. Figure 17 is an example of an exposure CDF for the North Saskatchewan River 1 km downstream of the Gold Bar WWTP. It represents the probability that a specific ammonia concentration will be exceeded. Reading the ammonia concentration from the bottom of the graph, for example, we can see that there is a 28% chance that ammonia concentrations will be greater than 0.02 mg/L 1 km from the outfall.

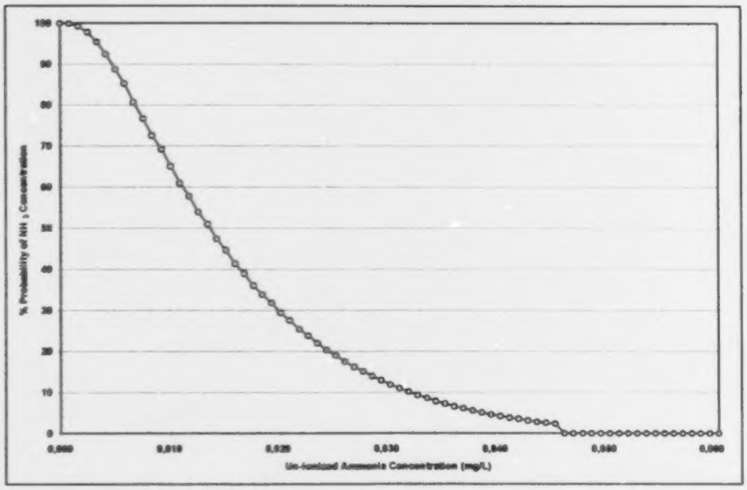

Figure 17: Cumulative density function of NH_3 concentrations for August at 1 km along the centre of the plume in the North Saskatchewan River

For each distance downstream of the North Saskatchewan River treatment plant, a risk curve was derived by combining the exposure CDF and the concentration–response relationship for percentage of biota adversely affected (as derived in the effects characterization). This was done by calculating the un-ionized ammonia concentration that caused effects ranging from 1 to 99% of species affected in 1% increments. Each effect concentration was then compared with the appropriate CDF for exposure to determine the proportion of the exposure values that exceeded the effects concentration. For 0% effect, 100% of the exposure values were greater; hence, each risk curve starts at 100% on the left-hand axis. Risk curves were generated for the centre-line plume 1, 2, 5, 10, 15 and 20 km downstream of the WWTP.

The risk curves are illustrated in Figures 18 to 23 and indicate that impact to aquatic organisms in the North Saskatchewan River decreases downstream of the outfall, as would be expected. For example, Figure 18 shows that at 1 km downstream, there is a 92.2% probability of at least 5% of the species exhibiting a 20% inhibition in growth or reproduction. However, at 20 km downstream, Figure 23 shows that there is a 9.8% probability of the same impact.

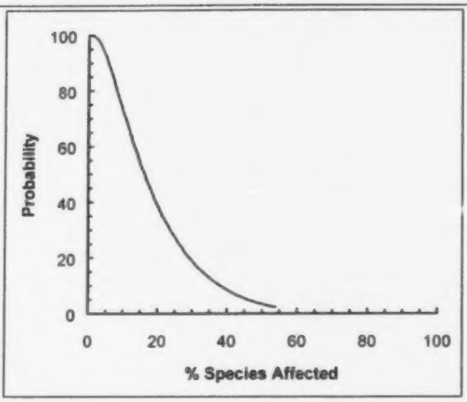

Figure 18: 1 km

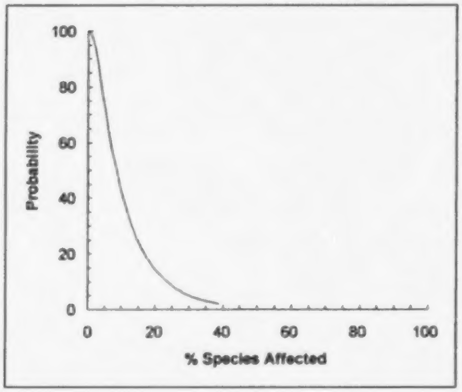

Figure 19: 2 km

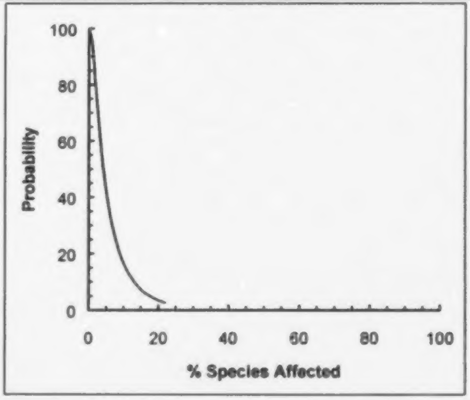

Figure 20: 5 km

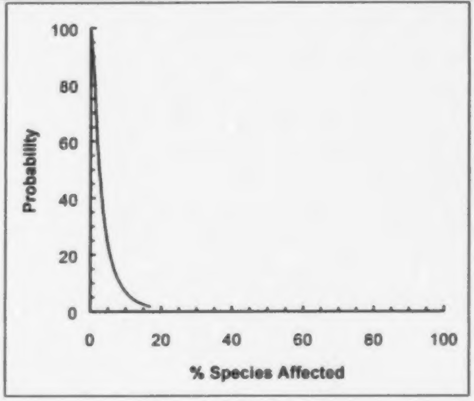

Figure 21: 10 km

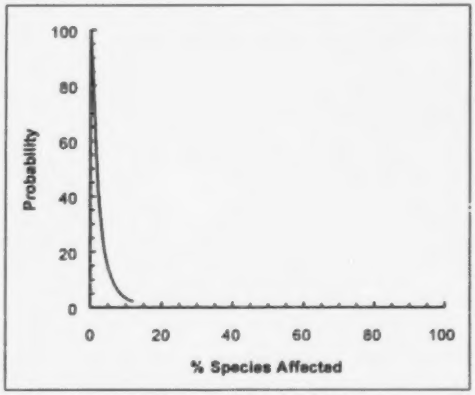

Figure 22: 15 km

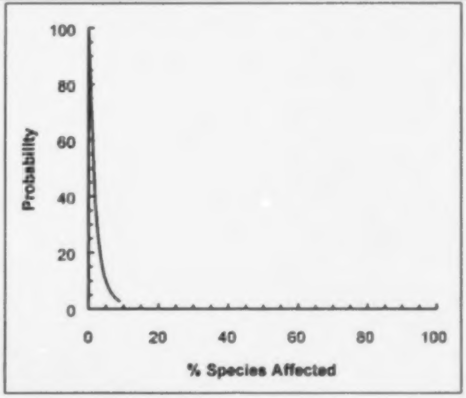

Figure 23: 20 km

Figures 18–23: Risk curves for 1–20 km downstream of the wastewater treatment plant on the North Saskatchewan River

Table 12 is a listing of probabilities of an effect (20% or greater reduction in growth/reproduction) to varying proportions of the aquatic community for each distance downstream of the WWTP for the month of August. This table shows that there is a decreasing probability of the defined toxic impact as more species are considered. For example, at 5 km, there is a 42% probability of an impact on 5% or more of the species, and there is a 0% probability of an impact on 25% or more of the species.

Table 12: Probability of species affected 1–20 km downstream of the wastewater treatment plant on the North Saskatchewan River in August

Distance from WWTP (km)	Prob. of 5% of species affected	Prob. of 10% of species affected	Prob. of 15% of species affected	Prob. of 20% of species affected	Prob. of 25% of species affected	Prob. of 50% of species affected
1	92	73	54	34	29	4
2	73	42	24	15	9	0
5	42	17	7	4	0	0
10	24	7	3	0	0	0
15	14	3	0	0	0	0
20	10	0	0	0	0	0

Figure 24 is a graphical representation of the impact gradient in the plume for 5% of species.

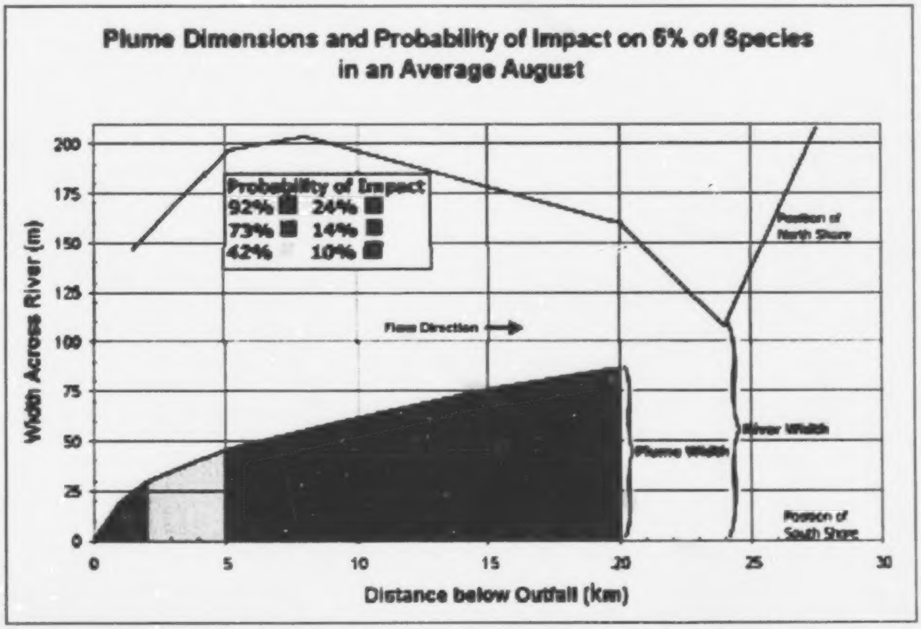

Figure 24: Probability of impacts in the North Saskatchewan River

This analysis is, however, a conservative estimate of risk to aquatic biota in the North Saskatchewan River for the month of greatest impact. The uncertainty in quantifying the risk from ammonia is discussed in Section 3.1.2.4.

The accuracy of CORMIX predictions when compared with field measurements is discussed in the supporting document (Environment Canada, 2000). Validation results showed that the greatest difference between the model and measured values lies within the first kilometre of the plume. From the discharge to 1000 m, the accuracy of predictions varies from 95% to 40% of measured, with no particular trend. The prediction improves with distance downstream; it is 98% accurate at 5300 m. Although the near-field zone is of less interest than the far-field zone for the risk assessment on the North Saskatchewan River, it is important to know that CORMIX significantly underestimates ammonia concentration in the first 1000 m.

From this analysis, there is a significant likelihood of an ecological impact from the release of ammonia in sewage effluent from Edmonton's sewage system in the summer months. In this Assessment Report, the chronic impact is a 20% decrease in the rate of growth or inhibition of reproduction. Significance can be quantified in the matrix of probabilities of impacts with distance downstream of the outfall (Table 12), such that we can predict that there is a 42% probability of a chronic impact on 5% or more of freshwater species in the North Saskatchewan River at 5 km below the outfall. This can be extended to predicting a 10% probability of this impact in a plume that is 20 km long by 80 m wide. The potential impacts are not likely to be as great in any other month, with very little impact expected from November to May.

The City of Edmonton is committed to reducing the ammonia concentration in its effluent to 5 mg/L in summer and 10 mg/L in winter by the year 2005 (Sawatzky, 1999).

3.1.2.3.3 Red River

The screening procedure for high ammonia concentrations in national rivers identified the Red River downstream of Winnipeg as a possibly impacted river (refer to the technical supporting document [Environment Canada, 2000]). Of the samples analysed by the province of Manitoba from 1988 to 1997, 27% of them exceeded the screening criteria of 0.02 mg un-ionized NH_3/L. This site was on the Red River at Selkirk, downstream of the Lockport Dam. The City of Winnipeg monitors water quality at the dam; 10% of samples were in excess of the chronic CTV of 0.04 mg un-ionized ammonia/L. These numbers warranted a detailed review of the data from the City of Winnipeg (data were provided by R. Ross, City of Winnipeg Water Pollution Control Centre, Chemistry Laboratory).

Winnipeg operates three sewage treatment plants: two on the Red River, called the South End Water Pollution Control Centre (SEWPCC) and the North End Water Pollution Control Centre (NEWPCC), and one on the Assiniboine River, called the West End Water Pollution Control Centre (WEWPCC). The CORMIX screening exercise identified the North End and West End plants as being potentially problematic (Figure 25).

The West End plant is the smallest of the three plants and discharges secondary-treated effluent to the Assiniboine River near the western boundary of the city. The South End plant is located in the southern half of the city (St. Vital) on the Red River. It handles the second largest volume of sewage.

The North End facility is the City of Winnipeg's largest-capacity plant, discharging to the Red River about 24 km downstream of the confluence with the Assiniboine River, near the northern boundary. Lockport Dam 20 km downstream backs up the water through Winnipeg, so that it has an average width of 175 m and an average depth of 3.5 m at low flow. As the river is relatively deep with slow currents, this leads to slow vertical mixing but rapid horizontal mixing. The Red River provides relatively low rates of dilution at full mixing, ranging from about 11:1 to 69:1 at low and average river flows, respectively.

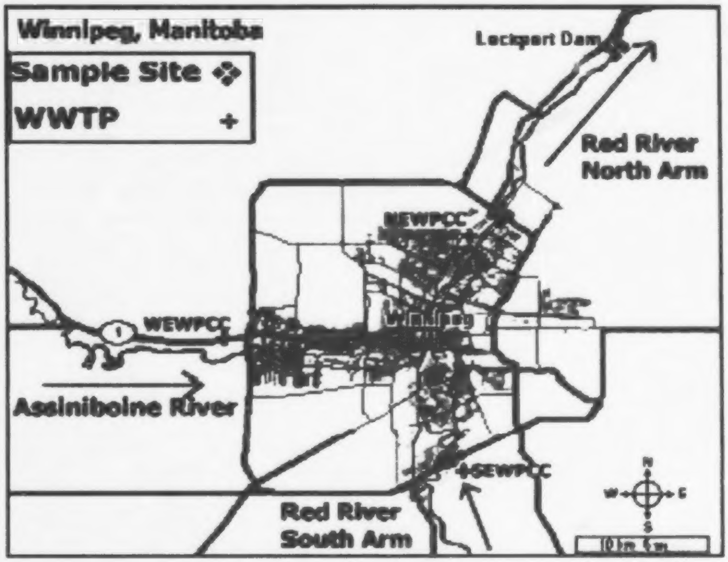

Figure 25: Winnipeg sewage treatment plants and sample sites

The City of Winnipeg monitors ammonia concentrations at four locations: (1) on the Assiniboine River at Winnipeg's Main Street Bridge, (2) on the Red River at Lockport Dam north of the city, (3) at Perimeter Bridge just north of the North End plant, and (4) at Winnipeg's Fort Garry Bridge downstream of the South End plant.

As shown in Figure 26, total ammonia concentrations have varied considerably at Lockport Dam, although the ammonia concentrations from the three WWTPs have not changed appreciably in the past 20 years. The City of Winnipeg did not change its sewage treatment processes during the period of data presented (1986–1997) in Figure 26 (Ross, 1998). A comparison of river flow data for the Red River with the total ammonia concentration at Lockport shows a weak negative correlation (–0.34).

There are some distinct patterns identifiable for flow rates and total ammonia concentrations. The predominant ones are the periodic fluctuation in both flow rates and total ammonia concentrations. Flows peak in the spring, while total ammonia peaks in late summer. General trends can be observed between high ammonia concentrations and low flows for the years 1988–1991 and between low ammonia concentrations and high flows, exemplified by the years 1995–1997.

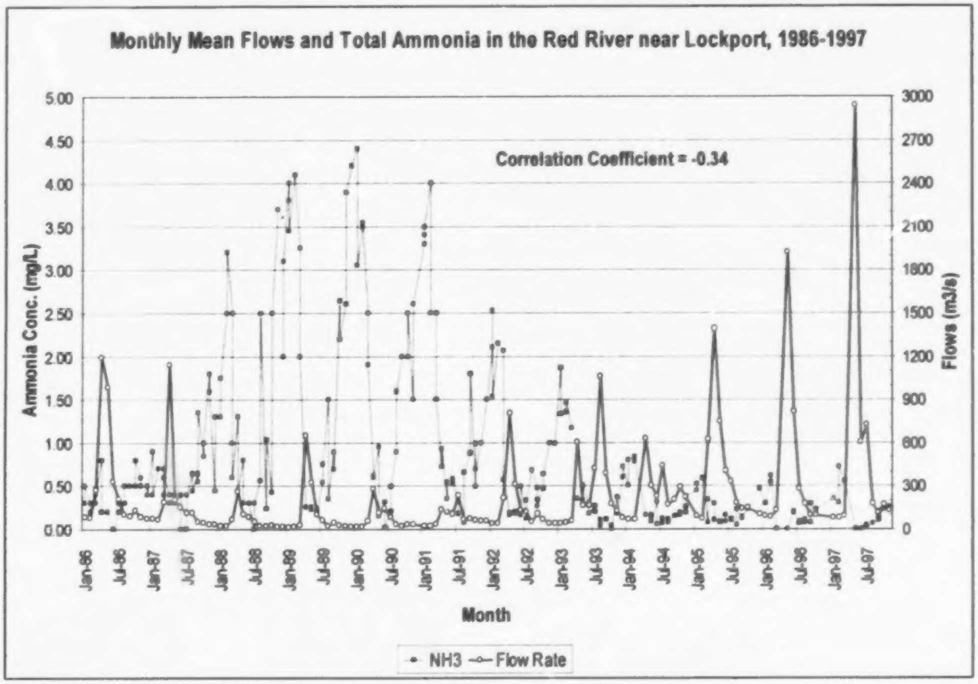

Figure 26: Red River monthly mean flows and total ammonia concentrations

The highest ammonia levels in the Red River occur from August to November. Therefore, this time frame was chosen for estimating risks to aquatic biota. Because the concern is for chronic effects, the appropriate temporal scale for estimating exposures is monthly (many chronic toxicity tests in fish are close to 1 month in length). In a chronic exposure scenario, high exposures on some days tend to be balanced out by low exposures on other days, such that overall exposure tends towards some measure of centrality. The appropriate measure of centrality in the case of ammonia concentrations in water is a geometric mean, because the underlying distribution for concentrations of contaminants in the environment is typically lognormal (Ott, 1995). Developing CDFs (probability of being in an exposure range versus ammonia concentration) for ammonia exposure also requires a measure of dispersion about the geometric mean of the ammonia concentration. Because we are concerned with chronic exposures, the measure of dispersion should not be used to estimate day-to-day variation. Rather, the dispersion measure should be used to account for year-to-year variability of the monthly mean. As the wastewater treatment practices and receiving environment conditions had not been significantly altered in the last decade, the long-term monitoring data were used to make predictions about possible exposures in the future. That is, the variation in monthly geometric means in the past 11 years can be used to estimate expected variation in the future. Therefore, for each sampling station and each month, exposure CDFs were developed as described in Appendix E.

At Lockport Dam, approximately 20 km north of the city (Figure 25), the un-ionized ammonia concentrations exceeded the CTV for most of the months from July to January for the period 1986–1993 (Figure 27, grab samples taken weekly). This is not the pattern seen at the North Perimeter station upstream. At Lockport Dam, the periods when the CTV are exceeded occur in both low and high water flow periods. The months of high concentrations extend from July occasionally to January. This may have something to do with the effect of the dam on flows in this area of the Red River.

From these data, it appears that a major factor in high ammonia levels downstream of Winnipeg is the flow rate of the Red River. The Lockport Dam creates a still-water area for some 20 km back past Winnipeg. The combination of moderately high pH (usually above 8) and warm temperatures in the Red River drives the un-ionized ammonia concentrations above 0.04 mg/L. The City of Winnipeg provided sufficient information from its water quality monitoring program to conduct an analysis to determine the probability of impacts.

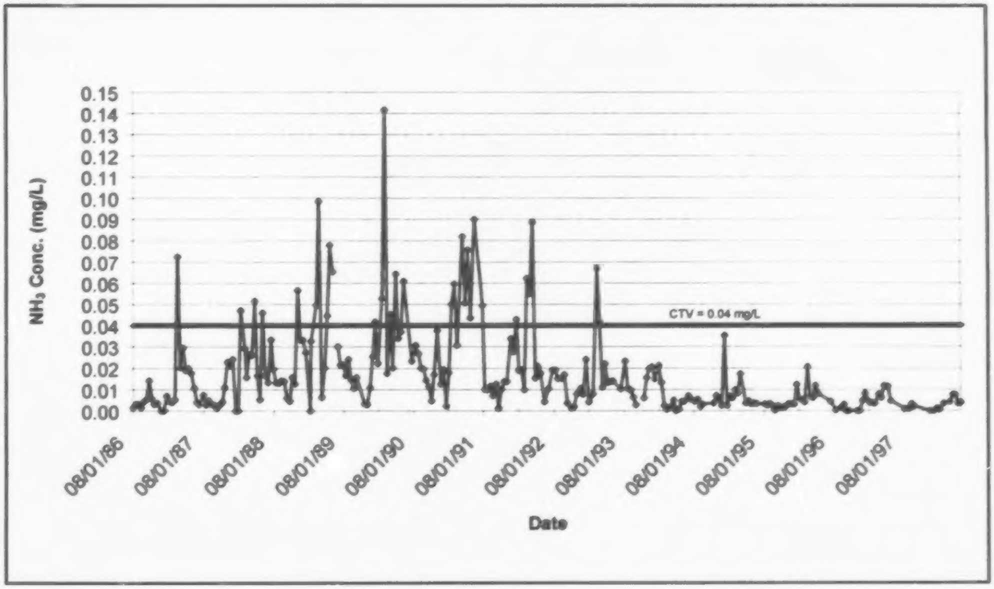

Figure 27: Un-ionized ammonia concentrations in the Red River at Lockport Dam, north of Winnipeg

For each of the four sampling stations, and for each month under consideration, a risk curve was derived by combining the exposure CDF (as derived from exposure characterization) and the concentration–response curve (as derived from effects characterization). This was done by calculating the un-ionized ammonia concentration that caused effects ranging from 1% to 99% of species affected in 1% increments. Each effect concentration was then compared with the appropriate CDF for exposure in order to determine the proportion of the exposure values that exceeded the effects concentration. For 0% effect or more, 100% of the exposure values were greater; hence, each risk curve starts at 100% on the left-hand axis. The risk curves are presented in Figures 28–43. A good point of comparison between the risk curves is the probability that 5% or more of the species will be affected by the ammonia in the river. For example, in August at the Lockport Dam site, there is a 24.4% probability of at least 5% of the species exhibiting a 20% inhibition in growth or reproduction.

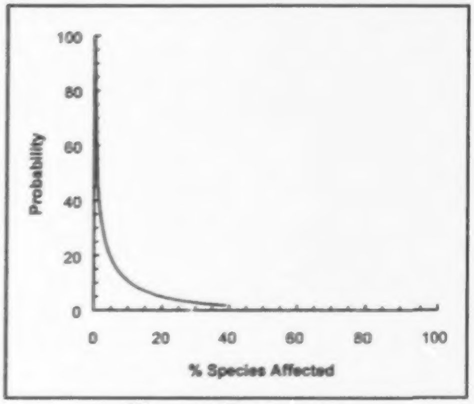

Figure 28: August

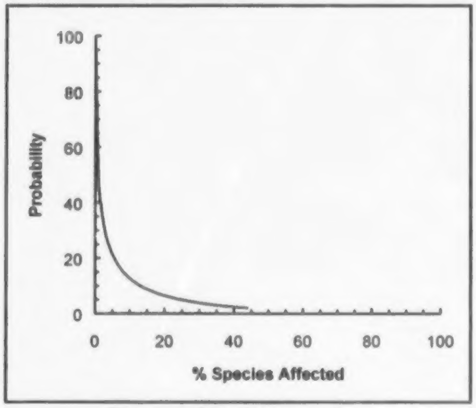

Figure 29: September

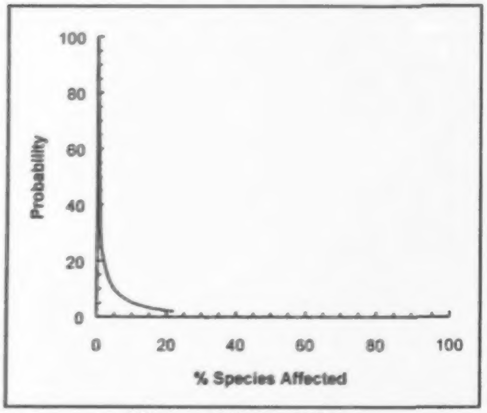

Figure 30: October

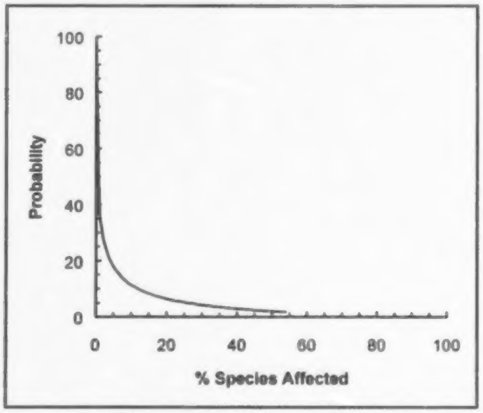

Figure 31: November

Figures 28–31: Risk curves for Fort Garry, Red River

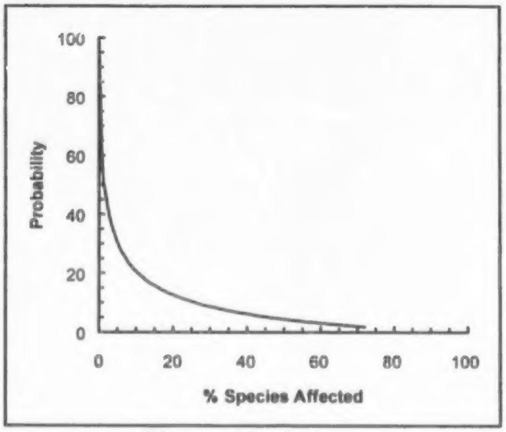

Figure 32: August

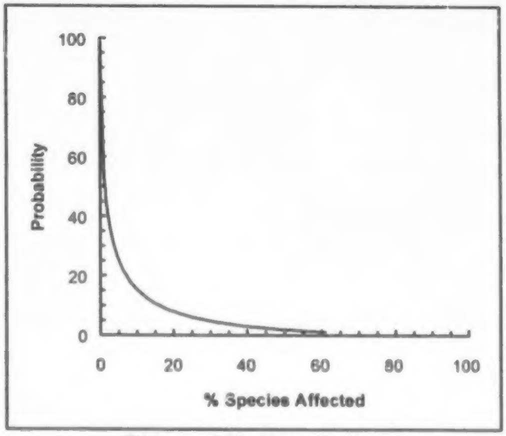

Figure 33: September

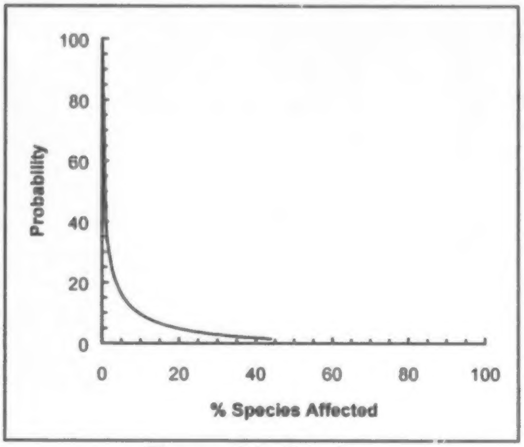

Figure 34: October

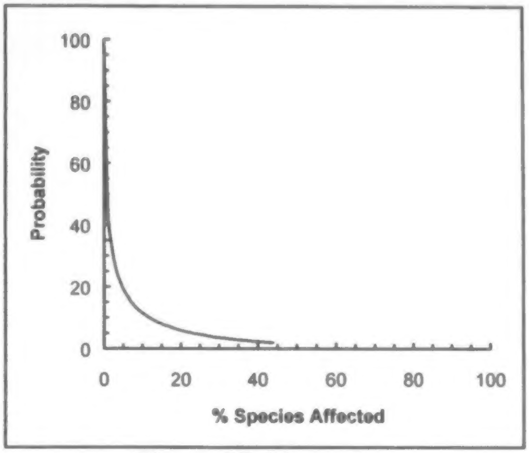

Figure 35: November

Figures 32–35: Risk curves for Perimeter Bridge, Red River

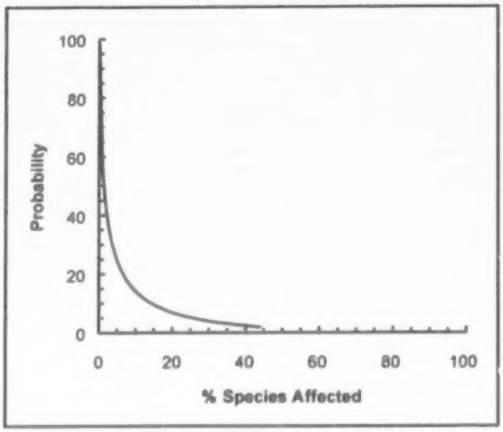

Figure 36: August

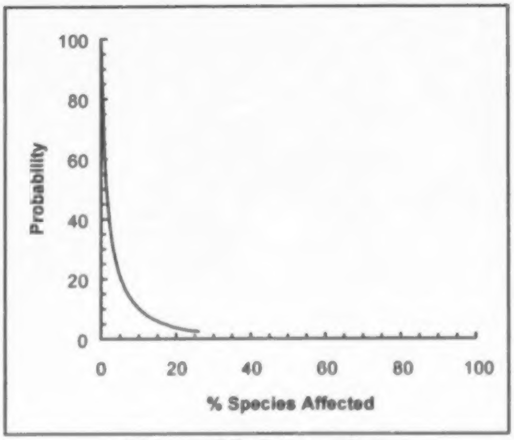

Figure 37: September

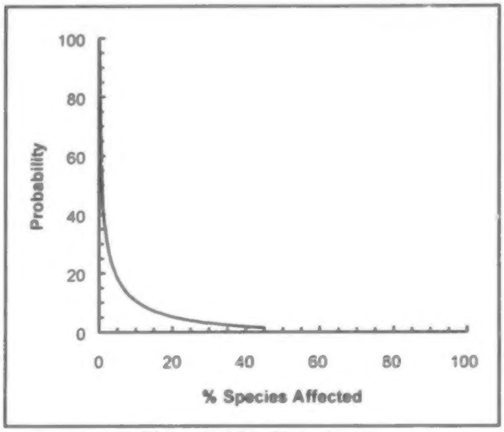

Figure 38: October

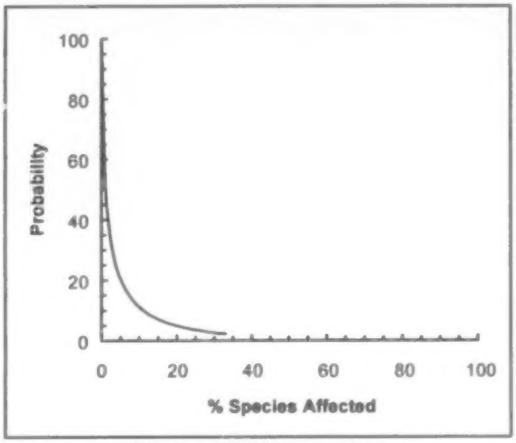

Figure 39: November

Figures 36–39: Risk curves for Lockport Dam, Red River

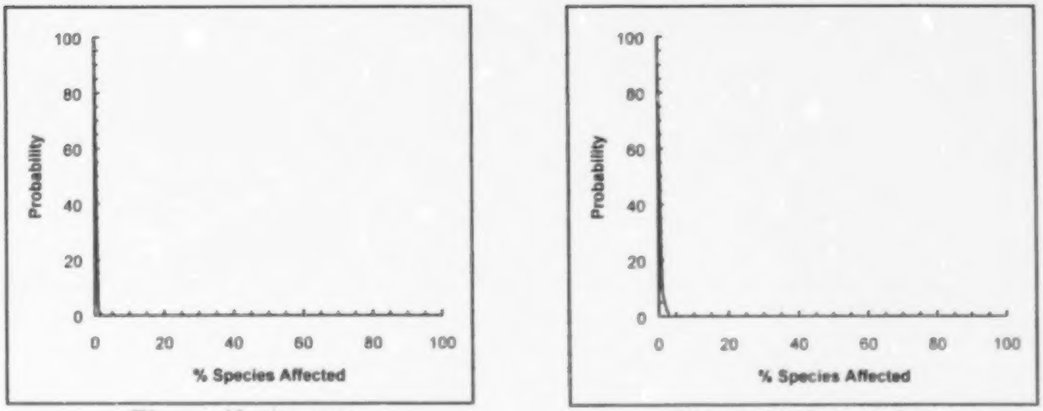

Figure 40: August

Figure 41: September

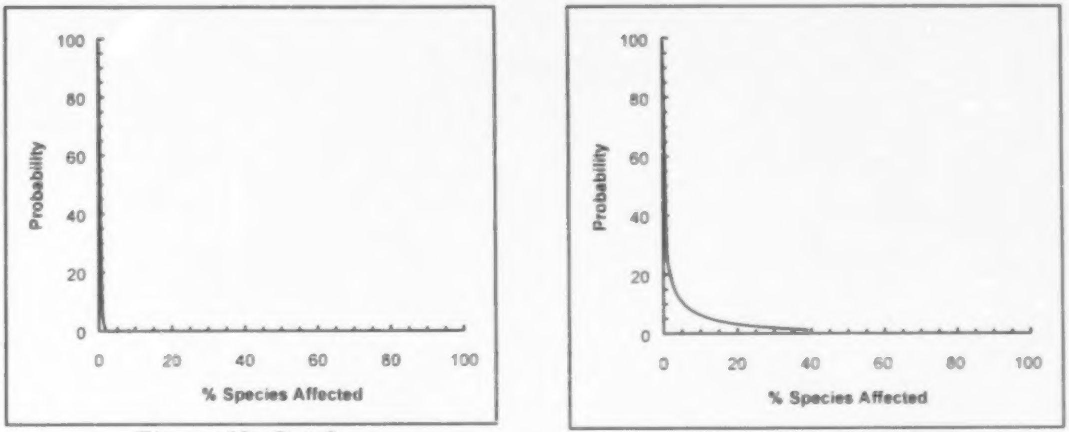

Figure 42: October

Figure 43: November

Figures 40–43: Risk curves at Main Street Bridge, Assiniboine River

Table 13 lists the probabilities of an effect (20% reduction in growth/reproduction) on varying proportions of the aquatic community for each month at the four monitoring sites in the Red and Assiniboine rivers.

Table 13: Probabilities of impacts at four sites around Winnipeg

Month	Probability of 5% of species affected	Probability of 10% of species affected	Probability of 15% of species affected	Probability of 20% of species affected	Probability of 25% of species affected
Red River — Fort Garry Bridge					
August	19	11	7	5	4
September	21	13	9	7	5
October	10	5	3	2	0
November	18	11	8	7	5
Red River — North Perimeter Bridge					
August	31	21	16	13	11
September	25	15	11	8	6
October	16	10	7	5	4
November	19	12	8	6	5
Red River — Lockport Dam					
August	24	14	10	7	5
September	21	10	6	4	3
October	18	11	7	5	4
November	20	11	7	5	4
Assiniboine River — Main Street Bridge					
August	0	0	0	0	0
September	0	0	0	0	0
October	0	0	0	0	0
November	11	6	4	3	3

From this analysis, there is a significant likelihood of an ecological impact from the release of ammonia in sewage effluent from Winnipeg's sewage system. In this assessment, the "toxic impact" is defined as a 20% decrease in the rate of growth or inhibition of reproduction. Significance can be quantified in that probabilities of impacts to the most sensitive 5% or more of freshwater species in the Red River are from 10% to 31%, depending on the month of exposure and the location. Probabilities of the same degree of impact to the most sensitive 10% or more of species range from 5% to 21%, depending on the month and location. The stretch of river encompassed by this study is roughly 30 km in length.

Significant impacts on freshwater biota in the Assiniboine River, roughly 20 km downstream of the discharge, are not likely, although some degree of impact might be expected at this site in November. Impacts upstream of the bridge could not be quantified.

The City of Winnipeg is currently conducting a site-specific ecotoxicological assessment of its municipal effluents.

3.1.2.4 Discussion of uncertainty

Uncertainty analyses seek to describe and interpret lack of knowledge that may be present in the implementation or interpretation of a risk analysis. The goal of uncertainty analyses is to provide the risk manager with the most complete information available on the expected outcomes of exposures. In risk analysis, scientific uncertainty derives from many sources, including inadequate scientific knowledge, natural variability, measurement error, sampling error and incorrect assumptions. Uncertainty can also arise from model mis-specification, including errors in statistics, parameters and initial conditions and failure to appropriately capture expert judgement (SETAC, 1997).

There are several major sources of uncertainty associated with the environmental risk assessment of ammonia. The principal source of uncertainty is the estimation of a chronic CTV at the low end of the toxicity scale. In this case, it was estimated to be 0.041 mg/L, with 95% prediction limits of 0.02–0.06 mg/L, which is just below the lowest measured EC_{20} estimated from published toxicity studies. Other major sources of uncertainty are the period of actual exposure in fish, the application of a generic assessment to specific situations, the lack of recent ambient concentration data in most Canadian media, and the potential confounding toxicity from other components of sewage effluents.

Regarding environmental exposure, there could be concentrations of ammonia in Canada that are higher than those identified and used in this assessment. Limited data were available for ammonia levels in air where the largest Canadian releases occur. For example, ammonia deposition rates at present across Canada are relatively low, although they can be very high in certain locales, typically associated with intensive livestock operations (i.e., the Lower Fraser Valley).

Of the three case studies used for WWTPs, two, Hamilton Harbour and Winnipeg, had well-documented water quality monitoring studies, and Edmonton had an intense, short-term study to determine ammonia dispersion in the plume that enabled modelling of the plume under variable conditions.

Analysis of ammonia released from pore water by the disposal of dredged sediment suggests that marine species might be adversely affected. However, this analysis should be viewed with caution due to the paucity of data with respect to marine species.

Regarding effects of ammonia on aquatic and terrestrial organisms, uncertainty inevitably surrounds the extrapolation from available toxicity data to potential ecosystem effects. The ammonia assessment is based on a few well-done freshwater field studies, modelling and extrapolation from laboratory toxicity work. The relatively small number of organisms that can be routinely cultured and tested in laboratory toxicity studies leads to this uncertainty when extrapolating these toxicity results to responses of natural populations. That said, the Europeans have documented ecological changes in their sensitive ecosystems likely as a result of the atmospheric deposition of ammonia. Canadian ecosystems will likely respond in similar ways.

To account for some of these uncertainties, conservative application factors were used as appropriate in the environmental risk analysis to derive ENEVs. An application factor is useful when few toxicity data are available and is, in general, environmentally protective, as it is a conservative approach. In addition, when there are many sources of uncertainty (e.g., sources of uncertainty in toxicity testing or exposure concentrations), application factors provide a relatively easy way to aggregate the multiple sources of uncertainty. In these cases, complicated statistical analysis may be impractical and costly.

The toxicity of ammonia to warm-water species is limited; however, the database for toxicity of ammonia to cold-water species is good . The problem of determining actual periods of exposure is difficult due to the mobility of many fish species in rivers. Toxicity estimation in the North Saskatchewan River is problematic due to the unrestricted nature of the river and the mobility of fish. However, benthic surveys above and below the outfall support the conclusion of toxicity from the sewage effluent, although not necessarily from ammonia. In the Red River, there is limited travel for fish below the Lockport Dam, and Hamilton Harbour has a greatly restricted water flow, with Lake Ontario restricting fish travel. Thus, the likelihood of overestimating risk to species critical to the structure and function of the community or ecosystem was judged to be acceptable.

The use of a generic group of aquatic species that are native to much of Canada may still present a source of uncertainty, for this group of species is not resident in all sewage discharge situations across Canada. Some of the species used were not commonly found in each of the three case studies, although they were all potentially resident. The use of site-specific assemblages of species would eliminate this uncertainty, although toxicity information is sparse for many species commonly found across Canada. A site-specific assemblage of species would not necessarily be less sensitive than the generic one chosen; some local species, mountain whitefish (*P. williamsoni*), for example, are more sensitive than rainbow trout (*O. mykiss*) to ammonia.

The major reviews of data conclude that pH has a larger effect than temperature on acute toxicity (WHO, 1986; U.S. EPA, 1998). There are no proven correlations between temperature and chronic toxicity due to the paucity of data. The effect on this assessment of assuming that toxicity increases, rather than decreases, with temperature is to make the late summer/early fall months the critical periods, whereas the risk from toxicity may be more spread out from spring to fall. In this case, this assessment would underestimate toxicity from ammonia in some months and overestimate it in others.

The probabilistic approach used for the case studies allows for a quantitative estimation of risk (analysed as a distribution of effects and exposure concentrations) and therefore incorporates many of the uncertainties associated with the effects and exposure characterization discussed above. The largest source of uncertainty lies in the estimate of the CTV.

In addition to uncertainty in the exposure and effects data, biological and ecological uncertainty needs to be considered. This includes consideration of the potential for organisms such as plants to recover from exposure and the effects of multiple stressors that are likely present. Ammonia is a constant component of sewage, but the concentrations will vary considerably based on social fluctuations from the city generating the effluent. It has been shown that organisms will tolerate higher concentrations of ammonia if the exposure is pulsed, rather than constant. Sewage effluent is also a complex mixture and is released to a variety of different ecosystems that will respond differently. Typical ecosystems include coastal marine/estuary systems, lake systems, and small and large river systems. Potential impacts are not strictly from ammonia, but could also be from excess chlorine, chlorinated compounds, chloramines, biochemical oxygen demand, chemical oxygen demand and metals.

In the North Saskatchewan River below Edmonton, confounding toxicity could arise from chloramines, as the City of Edmonton chloraminates its drinking water and disinfects its sewage with chlorine. A PSL toxicity assessment of chloramines is being conducted, and chlorinated wastewater effluents have been determined to be CEPA "toxic" under the PSL assessment program. Dissolved oxygen is typically high in the river, so lack of oxygen is not likely a component of the toxicity "package." Excessive organic matter could also generate an enriched environment that some pollutant-tolerant organisms will find attractive.

Hamilton Harbour is seriously impacted by the many industries and cities lining its shores. The sediments are generally contaminated with metals, polychlorinated biphenyls and polycyclic aromatic hydrocarbons. The bottom waters of the harbour become anoxic in summer, likely due to a combination of poor water exchange with Lake Ontario, biological degradation of organic matter from sewage, nitrification of ammonia and biological degradation of sediments.

Winnipeg does not disinfect its sewage, so there are no problems with excessive chlorine. It uses chlorine for drinking water, however, so there may be excessive chlorine from this exposure as well as some short-term exposure to chloramines as chlorine and ammonia react. The Red River below Winnipeg is slow moving, but relatively deep. Some oxygen sag has been noted in previous surveys; however, excessive algal growth below the WWTPs augments this somewhat.

The information presented in this risk assessment shows that ammonia is a chemical of concern. However, it is important to remember that ammonia toxicity is being assessed independently of all other stressors, including other effects of ammonia, such as its effects as a nutrient on primary production and its effects on dissolved oxygen concentrations from nitrification and plant respiration.

3.1.2.5 Interpretation of ecological significance

The toxicity of ammonia downstream of a sewage outfall varies with many parameters, the most important of which are the concentration of ammonia in the effluent, the temperature of the water, the pH of the water, the flow rate of the water system and the flow rate of the effluent. Secondarily, the way in which the effluent enters the receiving environment is important; a multi-port diffuser dilutes the ammonia more rapidly in the water column so that it poses less of a risk than an effluent that enters a water system as a single plume. Discrete plumes from a point source tend to disperse slowly in water systems unless they are highly energetic, i.e., exposed to tides or strong currents. Temperature cannot be separated from the toxicity equation due to a lack of adequate information on the relative toxicity of ammonia at different temperatures.

The maximum risk of acute and chronic toxicity in an aquatic ecosystem downstream from a sewage outfall or other point source of ammonia occurs at a combination of low flows, high temperatures and high pH values, typically in late summer and early fall. The temperature and pH conditions will drive the proportion of un-ionized ammonia to chronically toxic levels, and the low flows ensure that there is not sufficient dilution capacity in the water system to accommodate the amount of ammonia present. The toxic risk is very low for waters all across Canada from December to April due to the low water temperatures and reduced pH levels. Most agricultural runoff of ammonia occurs in early spring before it can bind to soil and will not have a significant impact on aquatic ecosystems.

The ecological impact of ammonia in aquatic ecosystems is likely to occur through chronic toxicity to benthic invertebrates and fish populations as a result of reduced reproductive capacity and reduced growth of young. These are subtle impacts that will likely not be noticed for some time below an outfall. Typically what happens is a decline in the numbers of a sensitive species. Unless there is continual recruitment from unaffected populations, the affected population may die out over time. Toxic impacts on aquatic ecosystems can extend for many kilometres below a large sewage outfall. Impacts on fish populations are very difficult to determine due to the mobile nature of many fish species and to recruitment of fish from non-impacted areas. Benthic invertebrates are a much better indicator of impact, as they are not very mobile for much of their life cycle. Below the outfall at Edmonton, the diversity and benthic community structure were severely disrupted for over 20 km. Some of the pollution-sensitive insects did not make a comeback at 100 km downstream. It is difficult to determine if this impact is from ammonia, one of the other major components of sewage effluent, or a combination of factors.

Ammonia is a fundamental building block of life; as such, it is a nutrient for primary producers. Some terrestrial ecosystems in Europe, especially coniferous forests, moors and fens, are being seriously affected by excess nitrogen, much of which is in the form of ammonia. The ammonia raining down on the Netherlands, Belgium, Germany and the United Kingdom is largely from intensive agricultural operations. In these cases, the ecological disturbance is through terrestrial eutrophication and a toxic reaction to beneficial mycorrhizae symbiotically associated with tree roots. The nutritional balance of the ecosystems is being upset so that the existing dominant plants are being destroyed or pushed out by plants more capable of using nitrogen. This same phenomenon is not happening in Canada, as we have more space with which to dilute the ammonia, and we do not have as many sensitive ecosystems in close proximity to ammonia sources. That said, there are potential instances of this occurring in Canada, in particular in the Lower Fraser Valley.

Aquatic eutrophication is generally limited not by ammonia, but by phosphorus. This was confirmed recently by a joint review by Environment Canada, Fisheries and Oceans Canada and Agriculture and Agri-Food Canada. Therefore, there is little ecological impact from aquatic eutrophication due to excessive ammonia concentrations. It follows that at least one example of a nitrogen-impacted water system exists in Canada. The Qu'Appelle Lakes in Saskatchewan downstream of Regina are likely impacted by ammonia loadings. The City of Regina does not remove nitrogen from its sewage effluent.

Benthic organisms and aquatic macrophytes below the Edmonton WWTP have been severely affected by the effluents, a major component of which is ammonia. The distribution and abundance of many aquatic insects have been altered, and the growth of aquatic macrophytes increases dramatically downstream of the outfall. Much of this can be attributed to excessive nutrients, including ammonia.

Due to the interaction between receiving water pH and temperature, those waters most at risk from sewage-related ammonia are those that are routinely basic in pH with a relatively warm summer temperature combined with low flows. In Canada, winter temperatures, regardless of pH, are low enough to keep the formation of un-ionized ammonia below the toxic threshold. Potentially toxic conditions typically start in May and can continue through to early October, depending on the water system and the yearly variation in pH, temperature and dissolved oxygen. In general, waters potentially sensitive to ammonia from WWTPs are found in southern areas of Alberta, Saskatchewan and Manitoba; southern Ontario; and the south shore of Quebec.

Most of the urban populations in the Maritime provinces and British Columbia discharge to a large river (St. John River, Fraser River), to lakes or directly to the ocean. There is little information on, or evidence of, potentially significant impacts of these discharges on their receiving environments, due largely to the high dilution capacity of the water bodies.

3.2 CEPA 1999 64(b): Environment upon which life depends

Ammonia does not deplete stratospheric ozone or contribute significantly to the formation of ground-level ozone, and its potential contribution to climate changes is negligible.

3.3 Proposed conclusions

CEPA 1999 64(a): Based on available data on releases of ammonia from municipal wastewater treatment plants and the aquatic conditions routinely found downstream of many such outfalls in Canada, it has been concluded that ammonia is entering the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity.

CEPA 1999 64(b): Based on available data, it has been concluded that ammonia is not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger to the environment on which life depends.

Proposed overall conclusion: Based on critical assessment of relevant information, it is proposed that ammonia be considered "toxic" as defined in Section 64 of CEPA.

3.4 Considerations for follow-up (further action)

The conclusion of this assessment is based on analyses of risks posed by releases of ammonia from municipal WWTPs. Priority should therefore be given to consideration of options to reduce exposure to ammonia from municipal wastewater systems. Since the toxicity of ammonia is dependent on many site-specific variables, options to reduce exposure to ammonia from municipal wastewater systems should be examined on a site-specific basis. If a city or region has a water body with a large dilution capacity, then ammonia control may not be necessary, or perhaps an improved dilution system may be required. If, however, there is not a sufficient dilution capacity, then additional treatment may be required. This typically takes the form of converting ammonia to nitrate. A further step of converting nitrate to nitrogen reduces the possibility of nitrate toxicity and oversupply of nutrients, but is considerably more costly.

Results of conservative screening-level assessments suggest that releases of ammonia from several other sources may also be causing environmental harm, but available data were insufficient to establish the extent and magnitude of such harm. It is therefore recommended that additional data be obtained to determine whether options to reduce exposure to ammonia from such sources should be undertaken. The following data needs are listed in order of priority:

- concentrations in waters receiving inputs of ammonia from strong industrial point sources,
- concentrations in Canadian streams and rivers receiving runoff from agricultural sources, including manure-fertilized fields and intensive livestock operations (feedlots and dairies),
- deposition of ammonia from the atmosphere, both in background areas and near point and area sources in Canada, and
- concentrations of ammonia in Canadian marine waters at municipal wastewater outfalls.

4.0 REFERENCES

Abeliovich, A. and Y. Azov. 1976. Toxicity of ammonia to algae in sewage oxidation ponds. Appl. Environ. Microbiol. 31(6): 801–806 (cited in U.S. EPA, 1985).

Aber, J.D., K.J. Nadelhoffer, P. Steudler and J.M. Melillo. 1989. Nitrogen saturation in northern forest ecosystems. BioScience 39: 378–386.

Alabaster, J., D. Shurben and G. Knowles. 1979. The effect of dissolved oxygen and salinity on the toxicity of ammonia to smolts of salmon, *Salmo salar* L. J. Fish Biol. 15: 705–712.

Allan, R.J., J.D.H. Williams, S.R. Joshi and W.F. Warwick. 1980. Historical changes and relationship to internal loading of sediment phosphorus forms in hypertrophic prairie lakes. J. Environ. Qual. 9: 199–206.

Anderson, A.-M., D. Trew, R. Neilson, N. MacAlpine and R. Borg. 1998a. Impacts of agriculture on surface water quality in Alberta: Haynes Creek study. Agricultural Impacts on Water Quality in Alberta, Technical Reports Vol. 1. Canada–Alberta Environmentally Sustainable Agriculture Agreement (CAESA), Alberta Agriculture.

Anderson, A.-M., D. Trew, R. Neilson, N. MacAlpine and R. Borg. 1998b. Impacts of agriculture on surface water quality in Alberta: provincial stream survey. Agricultural Impacts on Water Quality in Alberta, Technical Reports Vol. 1. Canada–Alberta Environmentally Sustainable Agriculture Agreement (CAESA), Alberta Agriculture.

Anderson, R., A. Anderson, A. Akena, J. Livingstone, A. Masuda, P. Mitchell, T. Reynoldson, D. Trew and M. Vukadinovic. 1986. North Saskatchewan River: characterization of water quality in the vicinity of Edmonton (1982–1983). Part I. Introduction, water chemistry, chlorophyll, bacteriology. Alberta Environmental Centre, Vegreville, Alberta.

Anlauf, K.G., J. Bottenheim, K. Brice, P. Fellin, H. Wiebe, R. Braman and G. Mackay. 1985. Measurement of atmospheric aerosols and photochemical products at a rural site in SW Ontario. Atmos. Environ. 19(11): 1859.

API (American Petroleum Institute). 1981. The sources, chemistry, fate and effects of ammonia in aquatic environments. Washington, D.C. 145 pp.

Asman, W. and A. Janssen. 1987. A long-range transport model for ammonia and ammonium for Europe. Atmos. Environ. 21(10): 2099–2119.

Asman, W.A., E. Pinksterboer, H. Maas, J.-W. Erisman, A. Waijers-Ypelaan, J. Slanina and T. Horst. 1989. Gradients of the ammonia concentration in a nature reserve: model results and measurements. Atmos. Environ. 23(10): 2259.

Bader, J.A. and J.M. Grizzle. 1992. Effects of ammonia on growth and survival of recently hatched channel catfish. J. Aquat. Anim. Health 4: 17–23.

Ball, I. 1967. The relative susceptibilities of some species of fresh-water fish to poisons — I. Ammonia. Water Res. 1: 767–775.

Barica, J. 1991. Deformation of the nitrogen cycle in a lake receiving excessive loadings of ammonia. Lakes Research Branch, National Water Research Institute, Environment Canada.

Barthelmie, R.J. and S.C. Pryor. 1998. Implications of ammonia emissions for fine aerosol formation and visibility impairment — A case study from the Lower Fraser Valley, British Columbia. Atmos. Environ. 32: 345–352.

Barthelmie, R.J. and S.C. Pryor. 1999. NH_x deposition to different surface types. Interim report to Environment Canada, Edmonton, March 1999 (unpublished).

Bassett, M. and J.H. Seinfeld. 1983. Atmospheric equilibrium model of sulfate and nitrate aerosols. Atmos. Environ. 17(11): 2237–2252.

Beauchamp, E., G. Kidd and G. Thurtell. 1982. Ammonia volatilization from liquid dairy cattle manure in the field. Can. J. Soil Sci. 62(1): 11–19.

Behra, P., L. Sigg and W. Stumm. 1989. Dominating influence of NH_3 on the oxidation of aqueous SO_2: the coupling of NH_3 and SO_2 in atmospheric water. Atmos. Environ. 23(12): 2691–2707.

Berthold, S. 1999. Personal communication. Quality Control Division, Greater Vancouver Regional District, Burnaby, British Columbia.

Bobbink, R., D. Boxman, E. Fremstad, G. Heil, A. Houdijk and J. Roelofs. 1992. Critical loads for nitrogen eutrophication of terrestrial and wetland ecosystems based upon changes in vegetation and fauna. *In:* P. Grennfelt and E. Thornelof (eds.), Critical loads for nitrogen — a workshop report. Nordic Council of Ministers, Copenhagen. pp. 111–159 (Report NORD 1992:41).

Borgmann, U. 1994. Chronic toxicity of ammonia to the amphipod *Hyalella azteca*; importance of ammonium ion and water hardness. Environ. Pollut. 86: 329–335.

Boxman, A., H. van Dijk, A. Houdijk and J. Roelofs. 1988. Critical loads for nitrogen with special emphasis on ammonium. *In:* J. Nilsson and P. Grennfelt (eds.), Critical loads for sulphur and nitrogen: report from a workshop held in Skokloster, Sweden, March 19–24, 1988. Nordic Council of Ministers, Copenhagen (Miljo Report 1988:15).

Bretthauer, R. 1978. Some ecological limits of tolerance to *Ochromonas sociabilis*. Verh. Int. Verein. Limnol. 20(3): 1850–1854 (cited in WHO, 1986).

Broderius, S. and L. Smith. 1979. Lethal and sublethal effects of binary mixtures of cyanide and hexavalent chromium, zinc, or ammonia to the fathead minow (*Pimephales promelas*) and rainbow trout (*Salmo gairdneri*). J. Fish. Res. Board Can. 36: 164–172.

Broderius, S., R. Drummond, J. Fiandt and C. Russom. 1985. Toxicity of ammonia to early life stages of the smallmouth bass at four pH values. Environ. Toxicol. Chem. 4: 87–96.

Brook, J., A. Wiebe, S. Woodhouse, C. Audette, T. Dann, S. Callaghan, M. Piechowski, E. Dabek-Zlotorzynska and J. Dloughy. 1997. Temporal and spatial relationships in fine particle strong acidity, sulphate, PM_{10}, and $PM_{2.5}$ across multiple Canadian locations. Atmos. Environ. 31: 4223–4236.

Brouwer, E., R. Bobbink, F. Meeuwsen and J. Roelofs. 1997. Recovery from acidification in aquatic mesocosms after reducing ammonium and sulphate deposition. Aquat. Bot. 56(2): 119–130.

Brown, V., D. Jordan and B. Tiller. 1969. The acute toxicity to rainbow trout of fluctuation concentrations and mixtures of ammonia, phenol and zinc. J. Fish Biol. 1: 1–9.

Buckley, J. 1978. Acute toxicity of un-ionized ammonia to fingerling coho salmon. Prog. Fish Cult. 40(1): 30–32.

Burkhalter, D. and C. Kaya. 1977. Effects of prolonged exposure to ammonia on fertilized eggs and sac fry of rainbow trout (*Salmo gairdneri*). Trans. Am. Fish. Soc. 106: 470–475.

Burkholder, J.M., E.J. Noga, C.W. Hobbs, H.B. Glasgow, Jr. and S.A. Smith. 1992. New "phantom" dinoflagellate is the causative agent of major estuarine fish kills. Nature 358: 407–410; Nature 360: 768 (correction to article).

Bytnerowicz, A. and M.E. Fenn. 1996. Nitrogen deposition in California forests: A review. Environ. Pollut. 92(2): 127–146.

Bytnerowicz, A. and G. Riechers. 1995. Nitrogenous air pollutants in a mixed conifer stand of the western Sierra Nevada, California. Atmos. Environ. 29(12): 1369–1377.

Calamari, D., R. Marchetti and G. Vailati. 1981. Effects of long-term exposure to ammonia on the developmental stages of rainbow trout (*Salmo gairdneri* Richardson). Rapp. P.-V. Reun., Cons. Int. Explor. Mer 178: 81–86.

Caraco, N.F. 1995. Influence of human populations on P transfers to aquatic systems: a regional scale study using large rivers. *In:* H. Tiessen (ed.), Phosphorus in the global environment. John Wiley, New York, N.Y. pp. 235–244.

Cardin, J. 1986. Memorandum to D. Hansen. U.S. Environmental Protection Agency, Narragansett, Rhode Island [cited in U.S. EPA, 1989].

CCREM (Canadian Council of Resource and Environment Ministers). 1987. Canadian water quality guidelines. Environment Canada, Ottawa, Ontario.

CFI (Canadian Fertilizer Institute). 1997. Environmental report card. Ottawa, Ontario.

Chambers, P.A. 1989. Reconnaissance study of the Qu'Appelle Lakes. Report on the September 1989 evaluation of aquatic macrophyte growth in the Qu'Appelle Lakes. National Hydrology Research Institute, Environment Canada (NHRI Contribution No. 89090).

Chambers, P., E. Prepas, M. Bothwell and H. Hamilton. 1989. Roots versus shoots in nutrient uptake by aquatic macrophytes in flowing waters. Can. J. Fish. Aquat. Sci. 46: 435–439.

Chambers, P., K. Kent, M. Charlton, M. Guy, C. Gagnon, E. Roberts, G. Grove and N. Foster. 2000. Nutrients and their impact on the Canadian environment. Draft report, National Water Research Institute, Environment Canada.

Charlton, M. 1997. Personal communication. Project Chief, Lake Remediation, National Water Research Institute, Environment Canada, Burlington, Ontario, April 18, 1997.

Charlton, M. and J. Milne. 1999. Ammonia in Hamilton Harbour 1998. Draft report produced in partnership with the Regional Municipality of Halton and the Regional Municipality of Hamilton-Wentworth. National Water Research Institute, Environment Canada, Burlington, Ontario, March 1999.

Cheng, L. and R.P. Angle. 1996. Model-calculated interannual variability of concentration, deposition and transboundary transport of anthropogenic sulphur and nitrogen in Alberta. Atmos. Environ. 30(23): 4021–4030.

Cheung, Y. and M. Wong. 1993. Toxic effects of dredged sediments of Hong Kong coastal waters on clams. Environ. Technol. 14: 1047–1055.

Chu, B. 1997. Unpublished Canadian water quality data. Environmental Conservation Branch, Environment Canada, Regina, Saskatchewan.

Clark, B. 1999. Letter to M. Guy, Environment Canada, concerning City of Saskatoon wastewater treatment plant mg NH_3 as N/L results (monthly averages), final effluent, dated January 15, 1999.

Cole, J.J., B.L. Peierls, N.F. Caraco and M.L. Pace. 1993. Nitrogen loading of rivers as a human-driven process. *In:* M.J. McDonnell and S.T.A. Pickett (eds.), Humans as components of ecosystems. Springer-Verlag, New York, N.Y. pp. 141–157.

Colt, J. and G. Tchobanoglous. 1978. Chronic exposure of channel catfish, *Ictalurus punctatus*, to ammonia: effects on growth and survival. Aquaculture 15: 353–372.

Cooke, S. 1996. Phosphorus and nitrogen dynamics in streams draining agricultural and aspen dominated forest watersheds in the boreal plain. M.Sc. thesis, Department of Biological Sciences, University of Alberta, Edmonton, Alberta.

Craig, G. 1999. Ammonia sublethal toxicity data. Unpublished report, prepared for Environment Canada, Edmonton, Alberta.

Daniel, T., R. Wendt, P. McGuire and D. Stoffel. 1982. Nonpoint source loading rates from selected land uses. Water Resour. Bull. 19(1): 117–120.

de Bode, M. 1990. Odour and ammonia emissions from manure storage. *In:* V. Nielsen, J. Voorburg and P. L'Hermite (eds.), Odour and ammonia emissions from livestock farming. Elsevier Applied Science, London.

DeCoursey, P. and W. Vernberg. 1975. The effect of dredging in a polluted estuary on the physiology of larval zooplankton. Water Res. 9: 149–154.

Dederen, L. 1992. Marine eutrophication in Europe: Similarities and regional differences in appearance. Sci. Total Environ. 6 (Suppl.): 663–672.

Demal, L. 1983. An intensive water quality survey of stream cattle access sites. Stratford/Avon River Environmental Management Project. Upper Thames River Conservation Authority, London, Ontario (Technical Report R-19).

Denmead, O., J. Simpson and J. Freney. 1977. A direct field measurement of ammonia emission after injection of anhydrous ammonia. Soil Sci. Soc. Am. J. 41: 1001–1004 [cited in Freney *et al.*, 1982].

Denmead, O, J. Freney and J. Simpson. 1982. Atmospheric dispersion of ammonia during application of anhydrous ammonia fertilizer. J. Environ. Qual. 11(4): 568–572.

Department of Scientific and Industrial Research. 1967. Chronic toxicity of ammonia to rainbow trout. *In:* Effects of pollution on fish. Report of the Director, 1967. Water Pollution Research Board. Her Majesty's Stationery Office, London. pp. 56–65.

De Vries, W. 1992. Empirical data and model results for critical nitrogen loads in the Netherlands. *In:* P. Grennfelt and E. Thornelof (eds.), Critical loads for nitrogen — a workshop report. Nordic Council of Ministers, Copenhagen. pp. 383–402 (Report NORD 1992:41).

Diamond, J., D. Mackler, W. Rasnake and D. Gruber. 1993. Derivation of site-specific ammonia criteria for an effluent-dominated headwater stream. Environ. Toxicol. Chem. 12: 649–658.

Dillon, P., L. Molot and W. Scheider. 1991. Phosphorus and nitrogen export from forested stream catchments in central Ontario. J. Environ. Qual. 20: 857–864.

Doneker, R. and G. Jirka. 1990. Expert system for hydrodynamic mixing zone analysis of conventional and toxic submerged single port discharges (CORMIX1). Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia (Technical Report EPA/600/3-90/012).

Downing, K. and J. Merkens. 1955. The influence of dissolved oxygen concentrations on the toxicity of un-ionized ammonia to rainbow trout (*Salmo gairdneri* Richardson). Ann. Appl. Biol. 43(2): 243–246.

Doyle, G.J., E. Tuazon, R. Graham. T. Mischke, A. Winer and J. Pitts. 1979. Simultaneous concentrations of ammonia and nitric acid in a polluted atmosphere and their equilibrium relationship to particulate ammonium nitrate. Environ. Sci. Technol. 13(11): 1416.

Duarte, C. 1995. Submerged aquatic vegetation in relation to different nutrient regimes. Ophelia 4[illegible] 87–112.

Dupont, J. 1998. Unpublished water quality data. Ministère de l'Environnement et de la Faune du Québec, Québec, Quebec.

ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals). 1994. Ammonia emissions to air in western Europe. Brussels (Technical Report No. 62).

Emerson, K., R. Lund, R. Thurston and R. Russo. 1975. Aqueous ammonia equilibrium calculations: effect of pH and temperature. J. Fish. Res. Board Can. 32: 2379–2383.

Environment Canada. 1984. Manual for spills of hazardous materials. Technical Services Branch, Environmental Protection Programs Directorate. 158 pp.

Environment Canada. 1997a. Environmental assessments of Priority Substances under the *Canadian Environmental Protection Act*. Guidance manual version 1.0 — March 1997. Chemicals Evaluation Division, Commercial Chemicals Evaluation Branch, Hull, Quebec (EPS 2/CC/3E).

Environment Canada. 1997b. Wastewater collection systems survey. Unpublished data. Ottawa, Ontario.

Environment Canada. 1997c. Municipal Water Use Database (MUD), 1996. Ottawa, Ontario.

Environment Canada. 2000. *Canadian Environmental Protection Act* — Priority Substances List — Supporting document for the environmental assessment of ammonia in the aquatic environment. Commercial Chemicals Evaluation Branch, Hull, Quebec.

Esmen, N. and R.B. Fergus. 1977. A qualitative analysis of atmospheric reactions between SO_2 and NH_3. Sci. Total Environ. 8(1): 69–77.

Evans, D. 1984. The roles of gill permeability and transport mechanisms in euryhalinity. *In:* W.S. Hoar and D.J. Randall (eds.), Fish physiology. Vol. XB. Academic Press, New York, N.Y. pp. 239–283.

Fangmeier, A., A. Hadwiger-Fangmeier, L. Van der Eerden and H.-J. Jaeger. 1994. Effects of atmospheric ammonia on vegetation — A review. Environ. Pollut. 86(1): 43–82.

Fekete, K. and L. Gyenes. 1993. Regional scale transport model for ammonia and ammonium. Atmos. Environ. 27A(7): 1099–1104.

Fenn, L. and L. Hossner. 1985. Ammonia volatilization from ammonium or ammonium forming nitrogen fertilizers. Springer-Verlag, New York, N.Y. Adv. Soil Sci. 1: 123–169.

Feth, J. 1966. Nitrogen compounds in natural waters. A review. Water Resour. Res. 2: 41–58.

Fisher, D., A. Gambell, G. Likens and F. Burmann. 1968. Atmospheric contributions to water quality of streams in the Hubbard Brook Experimental Forest, New Hampshire. Water Resour. Res. 4: 1115–1126.

Freney, J., J. Simpson and O. Denmead. 1982. Volatilization of ammonia. *In:* J. Freney and J. Simpson (eds.), Gaseous loss of nitrogen from plant–soil systems. Martinius Nijhoff/Dr. W. Junk Publishers, The Hague. Dev. Plant Soil Sci. 9: 1–32.

Gangbazo, G., A. Pesant, G. Barnett, J. Charuest and D. Cluis. 1995. Water contamination by ammonium nitrogen following the spreading of hog manure and mineral fertilizers. J. Environ. Qual. 24: 420–425.

Gartner Lee Ltd. 1998. Chloramine distribution in treated sewage effluent. Unpublished report prepared for the Commercial Chemicals Evaluation Branch, Environment Canada, North Vancouver, British Columbia.

Geadah, M. 1980. National inventory of natural and anthropogenic sources and emissions of ammonia. Environment Canada (Report EPS5/IC/1).

Gersich, F., D. Hopkins, S. Applegath, C. Mendoza and D. Milazzo. 1985. The sensitivity of chronic endpoints used in *Daphnia magna* Straus life-cycle tests. *In:* R.C. Bahner and D.J. Hansen (eds.), Aquatic toxicology and hazard assessment: eighth symposium. American Society for Testing and Materials, Philadelphia, Pennsylvania. Am. Soc. Test. Mater. Spec. Tech. Publ. 891: 245–252.

Gibson, A., T. Dillon and R. Engler. 1995. Naturally occurring levels of ammonia and sulfide in pore water: an assessment of the literature. U.S. Army Corps of Engineers Waterways Experiment Station (Technical Notes EEDP-01-34).

Giddens, J. 1975. Contamination of water by air pollutants, especially ammonia from animal manures. Department of Agronomy, University of Georgia, Athens, Georgia.

Gilliam, J., R. Daniels and K. Lutz. 1974. Nitrogen content of shallow groundwater in North Carolina Coastal Plain. J. Environ. Qual. 3: 147–151.

Gjessing, E.T. 1994. The role of humic substances in the acidification response of soil and water — results of the humic lake acidification experiment (Humex). Environ. Int. 20(3): 363–368.

Golder Associates. 1995. Joint Municipal–Industry North Saskatchewan River Study. Vols. 3 and 4. A report to the City of Edmonton.

Government of Canada. 1996. The state of Canada's environment — 1996. State of the Environment Reporting, Environment Canada, Ottawa, Ontario.

Gras, J. 1983. Ammonia and ammonium concentrations in the Antarctic atmosphere. Atmos. Environ. 17(4): 815–818.

Grayson, M. and D. Eckroth (eds.). 1978. Kirk-Othmer encyclopedia of chemical technology. 3rd edition. John Wiley & Sons, New York, N.Y.

Green, D. 1996. Surface water quality impacts following winter applications of hog manure in the InterLake Region, Manitoba, Canada, 1996. Water Quality Management, Manitoba Environment (Report No. 96-14).

Grindley J. 1946. Toxicity to rainbow trout and minnows of some substances known to be present in waste water discharged to rivers. Ann. Appl. Biol. 33(1): 103–112.

Hall, R.I., P.R. Leavitt, R. Quinlan, A.S. Dixit and J.P. Smol. 1999. Effects of agriculture, urbanization and climate on water quality in the northern Great Plains. Limnol. Oceanogr. 44: 739–756.

Halliwell, D. 1998. Unpublished water quality data. Environmental Conservation Branch, Environment Canada, Yellowknife, Northwest Territories.

Hampson, B. 1977. The analysis of ammonia in polluted sea water. Water Res. 11: 305–308.

Health Canada. 1999. *Canadian Environmental Protection Act*, Priority Substances List, Ammonia in the aquatic environment. Supporting documentation, health effects. Ottawa, Ontario.

Heil, G. and W. Diemont. 1983. Raised nutrient levels change heathland into grassland. Vegetation 53: 113–120.

Henry, J.L. 1995. Ammonia in the environment: a review of literature. Canadian Fertilizer Institute, Ottawa, Ontario.

Hermanutz, R., S. Hedtke, J. Arthur, R. Andrew and K. Allen. 1987. Ammonia effects on microinvertebrates and fish in outdoor experimental streams. Environ. Pollut. 47: 249–283.

Hoek, G., M. Mennen, G. Allen, P. Hofschreuder and T. van der Meulen. 1996. Concentrations of acidic air pollutants in the Netherlands. Atmos. Environ. 30(18): 3141–3150.

Hoff, J., D. Nelson and A. Sutton. 1981. Ammonia volatilization from liquid swine manure applied to cropland. J. Environ. Qual. 10(1): 90–95.

Hoff, R., M. Harwood, A. Sheppard, F. Froude, J. Martin and W. Strapp. 1997. Use of airborne LIDAR to determine aerosol sources and movement in the Lower Fraser Valley, BC. Atmos. Environ. 31: 2123–2134.

Howarth, R. 1988. Nutrient limitation of net primary production in marine ecosystems. Ann. Rev. Ecol. 19: 89–110.

Howarth, R.W., G. Billen, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J.A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarov, P. Murdoch and Z. Zhu. 1996. Regional nitrogen budgets and riverine inputs of N and P for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry 35: 75–139.

Howell, E.T., C.H. Marvin, R.W. Bilyea, P.B. Kauss and K. Sommers. 1996. Changes in environmental conditions during *Dreissena* colonization of a monitoring station in eastern Lake Erie. J. Great Lakes Res. 22(3): 744–756.

Hutchinson, G. and F. Viets, Jr. 1969. Nitrogen enrichment of surface water by absorption of ammonia volatilized from cattle feedlots. Science 166: 514–515.

Hutchinson, G., A. Mosier and C. Andre. 1982. Ammonia and amine emissions from a large cattle feedlot. J. Environ. Qual. 11(2): 288–293.

IRC Inc. 1997. Iona deep sea outfall 1996. Environmental monitoring program. Receiving water quality. Combined report. Prepared for Quality Control Division, Greater Vancouver Regional District, Burnaby, British Columbia.

Janzen, H., S. McGinn and E. Bremer. 1997. Identifying and exploiting non-fertilizer N inputs to spring wheat. Agriculture and Agri-Food Canada Research Station, Lethbridge, Alberta. Prepared for Alberta Agricultural Research Institute, Farming for the Future Research Program

Jennejohn, D., M. Newburger, K. Cheng and J. Wilkin. 1996. 1995 emission inventory of agricultural sources in British Columbia and the Lower Fraser Valley. Report prepared by Levelton and Associates for Environment Canada, Vancouver, British Columbia.

Jirka, G., P. Akar and J. Nash. 1996. Recent enhancements on the Cornell Mixing Zone Expert System, technical report, DeFrees Hydraulics Laboratory, Cornell University, Ithaca, New York (also to be published by Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia).

Jones, G., J. Nash and G. Jirka. 1996. CORMIX3: An expert system for mixing zone analysis and prediction of buoyant surface discharges. Technical report, DeFrees Hydraulics Laboratory, Cornell University, Ithaca, New York.

Jones, J., B. Borofka and R. Bachmann. 1976. Factors affecting nutrient loads in some Iowa streams. Water Res. 10: 117–122.

Kenney, B.C. 1990. Dynamics of phosphorus in a chain of lakes: the Fishing Lakes. National Hydrology Research Institute, Environment Canada, Burlington, Ontario (NHRI Paper No. 44; IWD Scientific Series No. 176).

Klemm, R. and J. Gray. 1982. Acidity and chemical composition of precipitation in central Alberta, 1977–1978. *In:* Proceedings: Acid Forming Emissions in Alberta and their Ecological Effect. Edmonton, Alberta, March 9–12, 1982.

Kohn, N.P., J.Q. Word, D.K. Niyogi, L.T. Ross, T. Dillon and D.W. Moore. 1994. Acute toxicity of ammonia to four species of marine amphipod. Mar. Environ. Res. 38: 1–15.

Korol, M. and G. Rattray. 1998. Canadian fertilizer consumption, shipments and trade 1996/1997. Farm Income Policy and Programs Directorate, Agriculture and Agri-Food Canada.

Lauriente, D. 1995. CEH marketing research report: Ammonia. Chemical Economics Handbook, SRI International.

Lekkerkerk, L., G. Heij and M. Hootsmans. 1995. Dutch Priority Programme on Acidification, Ammonia: the facts. Informatie en Kennis Centrum Landbouw and RIVM, Ministry of Housing, Spatial Planning and the Environment, The Hague (Report No. 300-06).

Lemon, E. and R. van Houtte. 1980 Ammonia exchange at the land surface. Agron. J. 72: 876–883 [cited in Freney *et al.*, 1982].

Liebhardt, W., C. Golt and J. Tupin. 1979. Nitrate and ammonium concentrations of ground water resulting from poultry manure applications. J. Environ. Qual. 8(2): 211–215.

Likens, G., F. Bormann, N. Johnson, D. Fisher and R. Pierce. 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in Hubbard Brook watershed ecosystem. Ecol. Monogr. 40(1): 1–24.

Lin, H. and D. Randall. 1991. Evidence for the presence of an electrogenic proton pump on the trout gill epithelium. J. Exp. Biol. 161: 119–134.

Lloyd, R. 1961. The toxicity of ammonia to rainbow trout (*Salmo gairdneri* Richardson). Water Waste Treatment J. 8: 278–279.

Lloyd, R. and D. Herbert. 1960. The influence of carbon dioxide on the toxicity of un-ionized ammonia to rainbow trout (*Salmo gairdneri* Richardson). Ann. Appl. Biol. 48(2): 399–404.

Lockyer, D. and B. Pain. 1989. Ammonia emissions from cattle, pig and poultry wastes applied to pasture. Environ. Pollut. 56: 19–30.

Lockyer, D. and D. Whitehead. 1990. Volatilization of ammonia from cattle urine applied to grassland. Soil Biol. Biochem. 22(8): 1137–1142.

Luebs, R., K. Davis and A. Laag. 1973. Enrichment of the atmosphere with nitrogen compounds volatilized from a large dairy area. J. Environ. Qual. 2(1): 137–141.

Manahan, S. 1994. Environmental chemistry. 6th edition. CRC Press, Inc., Boca Raton, Florida.

Marsalek, J. and H. Ng. 1989. Evaluation of pollution loadings from urban nonpoint sources: methodology and applications. J. Great Lakes Res. 15(3): 444–451.

Mayes, M., H. Alexander, D. Hopkins and P. Latvaitis. 1986. Acute and chronic toxicity of ammonia to freshwater fish: a site-specific study. Environ. Toxicol. Chem. 5: 437–442.

McCormick, J.H., S.J. Broderius and J.T. Fiandt. 1984. Toxicity of ammonia to early life stages of the green sunfish *Lepomis cyanellus* [with erratum]. Environ. Pollut. (Ser. A) 36: 147–163.

McDonald, K. 1999. Atmospheric case studies. Internal report. Environment Canada, Edmonton, Alberta.

McGinn, S. and R. Pradhan. 1997. Ammonia emissions from manure-amended soils. Energy Resource and Development Report, Lethbridge Research Centre, Agriculture and Agri-Food Canada.

MEFQ (Ministère de l'Environnement et de la Faune du Québec). 1998. *Évaluation de la toxicité des effluents des stations d'épuration municipales du Québec. Rapport d'étape. Campagne de caractérisation d'hiver.* Ministère de l'Environnement et de la Faune du Québec and Environment Canada, Montréal, Quebec.

Merkens, J. and K. Downing. 1957. The effect of tension of dissolved oxygen on the toxicity of un-ionized ammonia to several species of fish. Ann. Appl. Biol. 45: 521–527.

Ministers' Expert Advisory Panel. 1995. Report of the Ministers' Expert Advisory Panel on the second Priority Substances List under the *Canadian Environmental Protection Act* (CEPA). Government of Canada, Ottawa, Ontario. 26 pp.

Moller, D. and H. Schieferdecker. 1985. A relationship between agricultural NH_3 emissions and the atmospheric SO_2 content over industrial areas. Atmos. Environ. 19(5): 695–700.

Munroe, D.J. 1986. Qu'Appelle Fishing Lakes nutrient loading study, 1980 to 1983; final report. Environment Canada, Regina, Saskatchewan (WQB-WNR-86-02).

Nimmo, D., D. Link, L. Parrish, G. Rodriguez, W. Wuerthele and P. Davies. 1989. Comparison of on-site and laboratory toxicity tests: derivation of site-specific criteria for un-ionized ammonia in a Colorado transitional stream. Environ. Toxicol. Chem. 8: 1177–1189.

NPRI (National Pollutant Release Inventory). 1996. Summary report. Environment Canada, Minister of Supply and Services Canada (Catalogue No. En40-495/1-1996E).

NRC (National Research Council). 1979. Ammonia. Committee on Medical and Biological Effects of Environmental Pollutants, Division of Medical Sciences, Assembly of Life Sciences. University Park Press, Baltimore, Maryland.

NRC (National Research Council). 1993. Managing wastewater in coastal urban areas. Committee on Wastewater Management for Urban Coastal Areas. National Academy of Sciences, Washington, D.C.

Olson, B. Personal communication, September 9, 1997. Research Scientist, Alberta Agriculture, Lethbridge, Alberta.

OMEE (Ontario Ministry of Environment and Energy). 1997. Unpublished Provincial Water Quality Monitoring Network (PWQMN) data from 1994–1997. Environmental Monitoring and Reporting Branch.

Ott, W.R. 1995. Environmental statistics and data analysis. Lewis Publishers, Ann Arbor, Michigan.

Paerl, H. 1997. Coastal eutrophication and harmful algal blooms: Importance of atmospheric deposition and groundwater as "new" nitrogen and other nutrient sources. Limnol. Oceanogr. 42: 1154–1165.

Patni, N. 1991. Overview of land applications of animal manure in Canada. *In:* Proceedings of the National Workshop on Land Application of Animal Manure. Canadian Agricultural Research Council.

Paul, J. 1997. Ammonia emissions during hog production in Canada: cause for concern. Pacific Agri-Food Research Centre – Agassiz (Technical Report 134).

Peake, E. and R. Wong. 1992. An evaluation of precipitation measurements in Alberta (1978–1990). Final report to Environmental Quality Monitoring Branch, Environmental Assessment Division, Alberta Environment.

Pérez-Soba, M., T. Dueck, G. Puppi and P. Kuiper. 1995. Interactions of elevated CO_2, NH_3 and O_3 on mycorrhizal infection, gas exchange and N metabolism in saplings of Scots pine. Plant Soil 176: 107–116.

Pio, C., L. Castro, M. Cerqueira, I. Santos, F. Belchior and M. Salguerio. 1996. Source assessment of particulate air pollutants measured at the southwest European coast. Atmos. Environ. 30(19): 3309–3320.

Plass, M., H. Apsimon and B. Barker. 1993. A modeling study of the effect of ammonia on in-cloud oxidation and deposition of sulphur. Atmos. Environ. 27A(2): 223–234.

Poucher, S. 1986. Memorandum to D. Hansen. U.S. Environmental Protection Agency, Narragansett, Rhode Island [cited in U.S. EPA, 1989].

Pryor, S., R. Barthelmie, R. Hoff, S. Sakiyama, R. Simpson and D. Steyn. 1997a. REVEAL: characterizing fine aerosols in the Fraser Valley, B.C. Atmosphere-Ocean 35: 209–227.

Pryor, S., R. Hoff, R. Barthelmie and I. McKendry. 1997b. Vertical and horizontal heterogeneity of aerosol loadings: Observations and modeling. *In:* Proceedings of Air & Waste Management Association/AGU Specialty Conference on Visual Air Quality, Aerosols, and Global Radiation Balance. Air & Waste Management Association, Pittsburgh, Pennsylvania. pp. 516–528.

Pryor, S., R. Simpson, L. Guise-Bagley, R. Hoff and S. Sakiyama. 1997c. Visibility and aerosol composition in the Fraser Valley during REVEAL. J. Air Waste Manage. Assoc. 41(2): 147–156.

Przytocka-Jusiak, M. 1976. Growth and survival of *Chlorella vulgaris* in high concentrations of nitrogen. Acta Microbiol. Pol. 25(3): 185–197 [cited in WHO, 1986].

Quinn, P., R. Charlson and T. Bates. 1988. Simultaneous observations of ammonia in the atmosphere and ocean. Nature 335(6188): 336–338.

Rajagopal, R. 1978. Impact of land use on groundwater quality in the Grand Traverse Bay region of Michigan. J. Environ. Qual. 7: 93–98.

Randall, D.J. Unpublished. Ammonia production, excretion and toxicity in saltwater. Zoology Department, University of British Columbia, Vancouver, British Columbia.

Randall, D., J. Wilson, K. Peng, T. Kok, S. Kuah, S. Chew, T. Lam and Y. Ip. 2000. The mudskipper, *Periophthalmodon schlosseri*, actively transports NH_4^+ against a concentration gradient. Am. J. Physiol. In press.

Rankin, D. 1979. The influence of un-ionized ammonia on the long-term survival of sockeye salmon eggs. Department of Fisheries and Oceans, Nanaimo, British Columbia (Technical Report 912).

Reinbold, K. and S. Pescitelli. 1982. Effects of exposure to ammonia on sensitive life stages of aquatic organisms. Report to U.S. Environmental Protection Agency by Illinois Natural History Survey, Champaign, Illinois.

Rodgers, G., J. Vogt, D. Boyd, L. Simser, H. Lang, T. Murphy and D.S. Painter. 1992. Remedial action plan for Hamilton Harbour: environmental conditions and problem definition. 2nd edition. Canada–Ontario Agreement Respecting Water Quality.

Ross, R. 1998. Personal communication. City of Winnipeg Water Quality Laboratory, Winnipeg, Manitoba.

Ryan, A. 1998. Unpublished water quality data. Environmental Conservation Branch, Environment Canada, North Vancouver, British Columbia.

Ryden, J., D. Whitehead, D. Lockyer, R. Thompson, J. Skinner and E. Garwood. 1987. Ammonia emission from grassland and livestock production systems in the UK. Environ. Pollut. 48: 173–184.

Sawatzky, K. 1999. Personal communication. Asset Management and Public Works, City of Edmonton, Alberta.

Schjoerring, J., S. Husted and M. Poulsen. 1998. Soil–plant–atmosphere ammonia exchange associated with *Calluna vulgaris* and *Deschampsia flexuosa*. Atmos. Environ. 32: 507–512.

Schubauer-Berigan, M. and G. Ankley. 1991. The contribution of ammonia, metals and nonpolar organic compounds to the toxicity of sediment interstitial water from an Illinois River tributary. Environ. Toxicol. Chem. 10: 925–940.

Schulze, E., W. de Vries, M. Hauhs, K. Rosen, L. Rasmussen, C.-O. Tamm and J. Nilsson. 1989. Critical loads for nitrogen deposition on forest ecosystems. Water Air Soil Pollut. 48: 451–456.

Schuurkes, J. 1986. Atmospheric ammonium sulphate deposition and its role in the acidification and nitrogen enrichment of poorly buffered aquatic systems. Experientia 42: 351–357.

Schuurkes, J., I. Heck, P. Hesen, R. Leuven, J. Roelofs and H.C. Martin (eds.). 1986. Effects of sulphuric acid and acidifying ammonium deposition on water quality and vegetation of simulated soft water ecosystems. Proceedings of the International Symposium on Acidic Precipitation, Muskoka, Ontario, September 15–20, 1985. Water Air Soil Pollut. 31: 1–2.

Scott, W. and E. Crossman. 1973. Freshwater fishes of Canada. Fisheries Research Board of Canada (Bulletin 184).

Servant, J. and M. Delapart. 1983. Concentrations and origins of NO_3^- and NH_4^+ in oceanic air. *In:* CACGP Symposium on Tropospheric Chemistry with Emphasis on Sulphur and Nitrogen Cycles and the Chemistry of Clouds and Precipitation. August–September 1983, Oxford, England. 5th International Congress of the Commission on Atmospheric Chemistry and Global Pollution [cited in WHO, 1986].

Servizi, J.A., D.W. Martens and R.W. Gordon. 1978. Acute toxicity at Annacis Island primary sewage treatment plant. International Pacific Salmon Fisheries Commission (Progress Report No. 38).

SETAC (Society of Environmental Toxicology and Chemistry). 1997. Ecological risk assessment of contaminated sediments. Chapter 13. Critical issues in methodological uncertainty. Special Publication Series. SETAC Press, Pensacola, Florida.

Shaw, R., A. Trimbee, A. Minty, H. Fricker and E. Prepas. 1989. Atmospheric deposition of phosphorus and nitrogen in central Alberta with emphasis on Narrow Lake. Water Air Soil Pollut. 43: 119–134.

Sheppard, S.C. 1999. Effect of atmospheric ammonia on terrestrial plants — derivation of critical toxicity values. Unpublished report for Environment Canada, Edmonton, Alberta.

Sims, J. and D. Moore. 1995. Risk of pore water ammonia toxicity in dredged material bioassays. U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, Mississippi (Miscellaneous Paper D-95).

Smayda, T. 1997. Harmful algal blooms: their ecophysiology and general relevance to phytoplankton blooms in the sea. Limnol. Oceanogr. 42: 1137–1153.

Smith, W., T. Roush and J. Fiandt. 1984. Toxicity of ammonia to early life stages of bluegill (*Lepomis macrochirus*). Internal report, U.S. Environmental Protection Agency, Duluth, Minnesota (EPA-600/x-84-175).

Solbé, J. and D. Shurben. 1989. Toxicity of ammonia to early life stages of rainbow trout (*Salmo gairdneri*). Water Res. 23(1): 127–129.

Spotte, S. and G. Adams. 1983. Estimation of the allowable upper limit of ammonia in saline waters. Mar. Ecol. Prog. Ser. 10: 207–210.

Stewart, M., G. Marsh and S. Bertold. 1991. Iona deep sea outfall, 1991 environmental monitoring program, summary report. Quality Control Division, Greater Vancouver Regional District, Burnaby, British Columbia.

Suh, H.H., J.D. Spengler and P. Koutrakis. 1992. Personal exposures to acid aerosols and ammonia. Environ. Sci. Technol. 26(12): 2507–2517.

Swain, L. 1998. Personal communication. Unpublished water quality data for British Columbia. B.C. Ministry of Environment, Lands and Parks, Burnaby, British Columbia.

Swigert, J. and A. Spacie. 1983. Survival and growth of warmwater fishes exposed to ammonia under low flow conditions. U.S. Environmental Protection Agency, Washington, D.C.

Tchir, R. 1998. Unpublished water quality data for Alberta. Water Quality Branch, Alberta Environment.

Thurston, R.V. and R. Russo. 1983. Acute toxicity of ammonia to rainbow trout. Trans. Am. Fish. Soc. 112: 696–704.

Thurston, R.V., R. Russo and G. Phillips. 1983. Acute toxicity of ammonia to rainbow trout and fathead minnows. Trans. Am. Fish. Soc. 112(5): 696–710.

Thurston, R., G. Phillips, R. Russo and S. Hinkins. 1981a. Increased toxicity of ammonia to rainbow trout (*Salmo gairdneri*) resulting from reduced concentrations of dissolved oxygen. Can. J. Fish. Aquat. Sci. 38: 983–988.

Thurston, R., R. Russo and G. Vinogradov. 1981b. Ammonia toxicity to fishes: effect of pH on the toxicity of the un-ionized ammonia species. Environ. Sci. Technol. 15: 837–840.

Thurston, R., R. Russo, E. Meyn, R. Zajdel and C. Smith. 1986. Chronic toxicity of ammonia to fathead minnows. Trans. Am. Fish. Soc. 115: 196–207.

Timmons, D. and R. Holt. 1977. Nutrient losses in surface runoff from a native prairie. J. Environ. Qual. 6(4): 369–373.

Touchton, J. and W. Hargrove. 1982. Nitrogen sources and methods of application for no-tillage corn production. Agron. J. 74: 823–826.

UGLCC (Upper Great Lakes Connecting Channels Study Workgroup). 1988a. Geographic area report Detroit River (final report). Environment Canada, Toronto, Ontario.

UGLCC (Upper Great Lakes Connecting Channels Study Workgroup). 1988b. Geographic area report St. Clair River (final report). Environment Canada, Toronto, Ontario.

UGLCC (Upper Great Lakes Connecting Channels Study Workgroup). 1988c. Geographic area report St. Marys River (final report). Environment Canada, Toronto, Ontario.

UNEP (United Nations Environment Programme). Global programme of action for the [rotection of the marine environment from land-based activities. Intergovernmental Conference to Adopt a Global Programme of Action for the Protection of the Marine Environment from Land-Based Activities, October 23 – November 3, 1995, Washington, D.C. ((COA)/LBA/IG.2/7).

U.S. EPA (Environmental Protection Agency). 1985. Ambient water quality criteria for ammonia — 1984. Criteria and Standards Division, Washington, D.C. (EPA-440/5-85-001).

U.S. EPA (Environmental Protection Agency). 1989. Ambient water quality criteria for ammonia (saltwater). Washington, D.C. (EPA 440/5-88-004).

U.S. EPA (Environmental Protection Agency). 1994. Development and selection of ammonia emission factors. Washington, D.C. (EPA/600/R-94/190).

U.S. EPA (Environmental Protection Agency). 1998. Update of ambient water quality criteria for ammonia. Washington, D.C. (EPA 822-R-98-008).

Vamos, R. and R. Tasnadi. 1967. Ammonia poisoning in carp. 3. The oxygen content as a factor influencing the toxic limit of ammonia. Acta Biol. (Szeged) 13(3–4): 99–105.

Van der Eerden, L. 1982. Toxicity of ammonia to plants. Agric. Environ. 7(3–4): 223–236.

Van der Eerden, L., W. de Vries and H. van Dobben. 1998. Effects of ammonia deposition on forests in the Netherlands. Atmos. Environ. 32: 525–532.

Vezina, C. 1997. National ammonia inventory. Unpublished report, Pollution Data Branch, Environment Canada, Ottawa, Ontario.

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger and D.G. Tilman. 1997. Human alteration of the global nitrogen cycle: sources and consequences. Ecol. Appl. 7: 737–750.

Vollenweider, R.A. 1992. Coastal marine eutrophication: principles and control. *In:* R.A. Vollenweider, R. Marchetti and R. Viviani (eds.), Marine coastal eutrophication. Elsevier, Amsterdam.

Walker, R. 1998. Municipal effluent plume delineation modelling in selected Canadian rivers. A report to Toxic Substances Division, Environment Canada, Edmonton, Alberta. EBNFLO Environmental, Waterloo, Ontario.

WERF (Water Environmental Research Foundation). 1996. Aquatic ecological risk assessment: a multi-tiered approach (Version 2.0). Alexandria, Virginia (Project 91-AER-1).

Wetzel, R. 1983. Limnology. 2nd edition. CBS College Publishing, New York, N.Y.

WHO (World Health Organization). 1986. Ammonia. Geneva. 209 pp. (Environmental Health Criteria 54).

Williamson, D. 1998. Unpublished water quality data for Manitoba. Manitoba Environment.

Wilson, R., P. Wright, S. Munger and C. Wood. 1994. Ammonia excretion in freshwater rainbow trout (*Oncorhynchus mykiss*) and the importance of gill boundary layer acidification: lack of evidence for Na^+–NH_4^+ exchange. J. Exp. Biol. 191: 37–58.

Wright, P., D. Randall and S. Perry. 1989. Fish gill boundary layer: a site of linkage between carbon dioxide and ammonia excretion. J. Comp. Physiol. 158: 627–635.

Yamamoto, N., H. Nishiura, T. Honjo, Y. Ishikawa and K. Suzuki. 1995. A long-term study of atmospheric ammonia and particulate ammonium concentrations in Yokohama, Japan. Atmos. Environ. 29(1): 97–103.

Yesaki, T. and G. Iwama. 1992. Some effects of water hardness on survival, acid–base regulation, ion regulation and ammonia excretion in rainbow trout in highly alkaline water. Physiol. Zool. 65: 763–787.

Zebarth, B., J. Paul, R. van Kleeck and C. Watson. 1997. Impact of nitrogen management in agricultural production on water and air quality in the Lower Fraser Valley, British Columbia. Pacific Agri-Food Research Centre (Summerland), Agriculture and Agri-Food Canada (Technical Report No. 97-03).

APPENDIX A: AMMONIA EMISSIONS TO AIR FOR CANADA

Category/sector	1980 NH_3 emissions (tonnes)	1990 NH_3 emissions (tonnes)	*	1995 NH_3 emissions (tonnes)	*
Agricultural sources					
Animal husbandry					
Cattle and calves	108 078	257 383	A	331 016	A
Hogs and pigs	6 293	92 439	A	106 822	A
Sheep and lambs	525	2 468	A	2 492	A
Poultry		107 388	A	118 588	A
Horses		4 346	A	4 379	A
Fur animals (minks and foxes)		279	A	279	A
Animal husbandry total	114 896	464 304		563 576	
Fertilizer application					
Urea		86 081	A	109 232	A
Ammonium sulphate		3 070	A	4 183	A
Ammonium nitrate		2 292	A	2 199	A
Anhydrous ammonia	10 792	4 270	A	5 311	A
Nitrogen solutions		1 975	A	1 981	A
Monoammonium phosphate		4 565	A	4 948	A
Diammonium phosphate		2 213	A	1 562	A
Other phosphate fertilizer		9	A	0	A
Other fertilizer materials		2	A	1 925	A
Fertilizer application total	10 792	104 475		131 340	
Crops (vegetation)					
Crops total		NA		NA	
Agricultural total	**125 688**	**568 779**		**694 916**	
Non-industrial fuel combustion					
Power generation		492	B	528	A
Commercial fuel combustion		262	B	263	A
Residential fuel combustion	1 452	561	A	475	A
Residential wood fuel combustion		2 195	A	1 661	A
Non-industrial fuel combustion total	**1 452**	**3 509**		**2 927**	
Mobile sources					

Category/sector	1980 NH_3 emissions (tonnes)	1990 NH_3 emissions (tonnes)	*	1995 NH_3 emissions (tonnes)	*
Road transport		3 385	A	3 737	A
Rail transport		254	A	230	A
Air transport		304	A	310	A
Marine transport		203	A	192	A
Off-road use of fuel		608	A	658	A
Mobile sources total	**0**	**4 754**		**5 128**	
Industrial sources					
Fertilizer industry	64 277	38 705	B	10 784	A
Coke manufacturing (metallurgical)	718	464	P	NA	P
Petroleum refineries	3 653	3 538	P	4 664	P
Sodium carbonate	1 344			NA	
Chemical industry		NA		NA	
Petrochemical industry		NA		5 698	
Upstream oil and gas		NA		NA	
Miscellaneous industrial sources		NA		8 307	
Industrial fuel combustion		NA	B	463	A
Industrial fuel wood combustion		1 375	B	2 923	A
Industrial sources total	**69 992**	**44 082**		**32 839**	
Miscellaneous sources					
Incineration	306	252	A	355	A
Forest fires	15 911	2 989	A	15 023	A
Human	133	7 032	A	7 554	A
Cigarette smoking	6	5	A	5	A
Refrigeration		NA		NA	
Miscellaneous sources total	**16 356**	**10 279**		**22 936**	
Natural sources					
Biological litter	454 171	458 386	A	458 386	A
Wild animals	35 407	43 993	A	43 993	A
Biogenics (vegetation)		NA		NA	
Natural sources total	**489 578**	**502 379**		**502 379**	

Category/sector	**1980 NH_3 emissions (tonnes)**	**1990 NH_3 emissions (tonnes)**	*	**1995 NH_3 emissions (tonnes)**	*
Canadian total	**703 066**	**1 133 783**		**1 231 672**	
Canadian total (without natural)	**213 488**	**631 404**		**758 745**	

Source: Vezina (1997).

Notes:

NA = Not available at this date

* Data origin: P = point sources only, A = area sources, B = point and area sources

1990 Inventory: Sectors to be completed: Industrial sectors, Refrigeration and Vegetation (all)

1995 Inventory: Point sources are not available. Only area sources were done (some are preliminary).

1980 data are from Geadah (1980).

1990 and 1995 data use the same calculation methods.

APPENDIX B: PROVINCIAL BREAKDOWN OF AMMONIA RELEASES FROM NPRI (1996)

Province	**Quantity released (tonnes)**
Alberta	17 665
Ontario	7 552
Quebec	1 914
British Columbia	1 802
Manitoba	1 291
Saskatchewan	865
New Brunswick	789
Nova Scotia	106
Northwest Territories	41
Newfoundland	13
Prince Edward Island	None reported
Yukon	None reported

APPENDIX C: TOP 12 URBAN CENTRES FOR AMMONIA LOADING RATE (TONNES/YEAR) IN 1995 OR 1996

City	Province	Facility type	Average yearly effluent flow rate (million m^3/year)	Yearly avg. NH_3 conc. (mg/L)	NH_3 loading rate (tonnes/year)
Montréal Urban Community	QC	Primary	930	6.59	6128
Metro Toronto	ON	Tertiary	463	12.0	5938
Greater Vancouver	BC	Primary/secondary	432	14.0	5741
Winnipeg	MB	Secondary	83	26.02	2152
Metro Edmonton	AB	Secondary	91	21.42	1946
Hamilton	ON	Tertiary/secondary	115	13.00	1499
Longueuil	QC	Primary	114	9.79	1121
Calgary	AB	Tertiary/secondary	146	5.02	996
Metro Québec City	QC	Secondary	57	11.63	667
Victoria Region	BC	Primary	26	13.89	377
Burlington	ON	Tertiary	27	13.89	370
Saskatoon[1]	SK	Enhanced primary	30	11.78	352

[1] Saskatoon's loading rate was considerably less after May 1996, due to tertiary treatment. In 1998, they achieved an average ammonia concentration of 0.68 mg/L; the loading rate was approximately 21 tonnes/year (Clark, 1999).

APPENDIX D: DEVELOPMENT OF EXPOSURE CDFS FOR THE NORTH SASKATCHEWAN RIVER

The following steps were taken to enable development of exposure CDFs for the North Saskatchewan River.

- A rough sensitivity analysis was carried out to determine which input variables had the most influence on predicted ammonia levels in the river (see "Sensitivity analysis of river parameters on the size of the potentially toxic zone" in technical supporting document [Environment Canada, 2000]).

- Based on the results of the sensitivity analysis, five important input variables were identified; these were river flow, temperature, pH, effluent flow and total ammonia concentration. There were concerns with uncertainties about the monthly geometric mean for ammonia levels in the North Saskatchewan River. Thus, monthly arithmetic means were estimated for the normally distributed input variables (river temperature and pH) and monthly geometric means for the lognormally distributed variables (river and effluent flow, effluent ammonia concentration). Using the calculated means, normal distributions were fit to temperature and pH (the latter is already on a log scale), and lognormal distributions were fit to the remaining three input variables.

- For each of these five parameters, the available data were analysed to develop distributions of each. Each parameter distribution was then fed into a statistical package (i.e., Crystal Ball) to expand the distribution using Latin Hypercube sampling so as to develop a larger data set with which to make predictions. The measured correlations between the input variables (e.g., effluent flow and ammonia concentration) were specified prior to the sampling exercise.

- Five hundred sets of parameters were then developed and fed into CORMIX to develop predictions for a typical August at six distances downstream of the effluent outfall (1, 2, 5, 10, 15 and 20 km). The outputs from this exercise were 500 estimates of un-ionized ammonia levels (mid-plume) at each of several distances between 1 and 20 km downstream of the plant. Lognormal distributions were then fit to the data at each distance downstream.

- This distribution of data points was divided into ranges equal in size (each range was 0.000 58 units). The number of data points in each range was used to develop an exposure CDF for each of the distances (1, 2, 5, 10, 15 and 20 km) downstream of the Gold Bar WWTP.

APPENDIX E: DEVELOPMENT OF EXPOSURE CDFS FOR THE RED RIVER

The following steps were taken to enable development of exposure CDFs for the Red River from August to November.

- For each of August, September, October and November, geometric means were calculated for each year in the database (1986–1997) for each sampling station (see "Winnipeg water quality data" in the technical supporting document [Environment Canada, 2000]).
- For each month (n = 4) and sampling station (n = 4), a lognormal distribution was fit to the monthly geometric means for the period 1986–1996 using the statistical modelling program Crystal Ball. Once a lognormal distribution was fit, Crystal Ball was used with a Latin Hypercube sampling technique to expand each data set to 10 000 data points.

This expanded data set was split into a large number of small ranges equal in size. The number of data points in each range was tallied to develop a CDF for each month at each sampling site (as an example, see Figure 44).

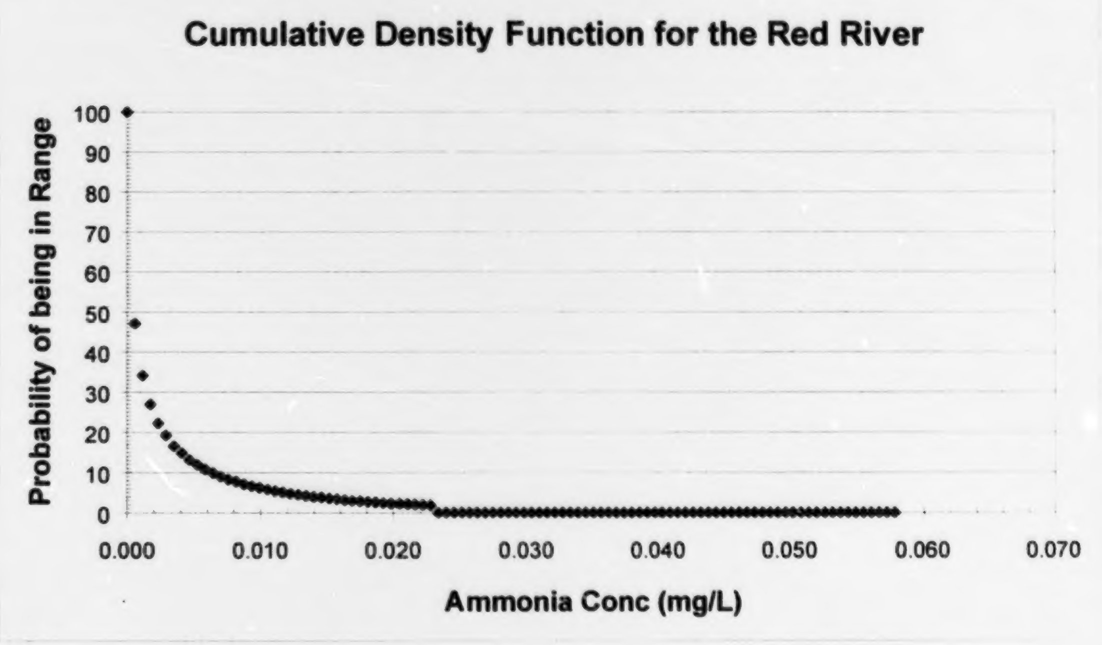

Figure 44: Cumulative density function for Red River at Fort Garry Bridge, August

APPENDIX F: SEARCH STRATEGIES EMPLOYED FOR IDENTIFICATION OF RELEVANT DATA

Environmental assessment

Data relevant to the assessment of whether ammonia in the aquatic environment is "toxic" to the environment under CEPA were identified from existing review documents, published reference texts and on-line searches conducted between January 1996 and January 1999. The following scientific databases were searched: Aquatic Science and Fisheries Abstracts (Cambridge Scientific Abstracts; 1978–1996), AQUIRE (Aquatic Toxicity Information Retrieval, U.S. Environmental Protection Agency), Biosis Previews (1969–1996), CESARS (Chemical Evaluation Search and Retrieval System, Ontario Ministry of the Environment and Michigan Department of Natural Resources), CHRIS (Chemical Hazard Release Information System, U.S. Coast Guard; 1964–1985), Current Contents (Institute for Scientific Information; 1996–1998), ELIAS (Environmental Library Integrated Automated System, Environment Canada library), Enviroline (R.R. Bowker Publishing Company; 1975–1996), Environmental Bibliography (1974–1995), MUD (Municipal Water Use Database, Environment Canada; 1996), NTIS (National Technical Information Service, U.S. Department of Commerce; 1964–1996), Pollution Abstracts (Cambridge Scientific Abstracts; 1970–1996) and RTECS (Registry of Toxic Effects of Chemical Substances, U.S. National Institute for Occupational Safety and Health), as well as water quality databases from Environment Canada, British Columbia, Alberta, Saskatchewan, Manitoba, Ontario, Quebec, Nova Scotia, New Brunswick and Newfoundland and Labrador and the National Pollutant Release Inventory (Environment Canada; 1994–1996). Searches were also performed between 1997 and 1999 on library systems across Canada. Surveys of Canadian industry and municipalities, other than in Quebec, were conducted to determine the use and release of ammonia. Additional relevant information was obtained voluntarily from municipalities and companies. Data obtained after January 1999 were not considered in this assessment.